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The Fulcher Bands of HD and D_2[1]

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(Received December 22, 1934)

First an account is given of the production and photography under high dispersion of the molecular spectra of H_2, HD and D_2 from the ultraviolet to the infrared. Besides the HD and D_2 lines many new H_2 lines were found. The Fulcher bands ($1s\sigma \cdot 3p\pi\ ^3\Pi \rightarrow 1s\sigma \cdot 2s\sigma\ ^3\Sigma$ transitions) are given and the constants of these bands compared for the three isotopic molecules. One component of the higher vibrational levels of the initial state is predissociated. From this it follows that the heat of dissociation of the normal molecule must lie between 4.43 and 4.52 volts.

THE discovery of the heavy hydrogen isotope deuterium has provided new possibilities for the study of the molecular spectrum of hydrogen. The available experimental material has tripled, for while we had hitherto only the spectrum of H_2 we now have also the spectra of HD and D_2. The spectra of these three molecules must be very similar in structure but with certain characteristic differences which result mainly from the different masses of the molecules. The study of these differences will furnish a more accurate and detailed test of the theory of band spectra and will permit a more precise evaluation of the molecular constants. Besides, and this is much more important, we can expect that the new spectra of HD and D_2 will be of great help for those parts of the H_2 spectrum which have so far defied analysis or for which the interpretation was uncertain. We have begun the study of the HD and D_2 spectra chiefly with the latter point in view, although the present paper is concerned chiefly with the former.

EXPERIMENTAL PROCEDURE

§1. The preparation of the hydrogen

For the greater part of the work the hydrogen gas was prepared by having small amounts of heavy water react in an evacuated glass tube with metallic sodium which had been distilled into it. The gas passed through an electrically heated palladium tube into the discharge tube. One drop of water was sufficient to run the discharge tube for many hundreds of hours. In the later stages of the experiments when we were anxious to work with D_2 which was as free as possible from HD and H_2, we used pure D_2 which had been obtained by electrolysis in the Princeton Chemical Laboratory.

The quartz discharge tube with tantalum electrodes has been described elsewhere.[3] It was usually operated with about 5000 volts and 0.8 ampere. The electrodes had a considerable

[1] The results of this paper were presented at the St. Petersburg meeting of the American Chemical Society in March, 1934, and a brief account of them appeared in Nature **133**, 611 (1934).

[2] National Research Fellow.

[3] G. H. Dieke and R. W. Blue, Phys. Rev. **45**, 395 (1934).

amount of H_2 adsorbed. We replaced this gradually by deuterium by admitting D to the tube and operating the tube for a considerable time with the electrodes being allowed to become as hot as possible. The gas then was pumped off, fresh deuterium gas admitted, and the process repeated until the mixture in the tube showed the desired deuterium concentration. This way of replacing the adsorbed H by D would be very inefficient if a very high D-concentration were required in the beginning. Baking out the electrodes in an induction furnace would then lead much quicker to the desired result. We needed, however, the spectrum at several intermediate concentrations and for this our method was most convenient. The D concentration was determined by measuring with the help of a step reducer the ratio of the intensities of $D\alpha$ and $H\alpha$.

§2. Photography of the spectrum

The spectrum was photographed in the first order of a 21 ft. grating with 30,000 lines per inch and a dispersion of about 1.3A per mm. The exposure times necessary to obtain an intense spectrum ranged from less than two hours in the violet to 24 hours or more in the red or infrared. For the region from $H\alpha$ toward the infrared the astigmatism of the grating reduced the intensity so much that good exposures could no more be obtained with reasonable exposure times. By the use of a suitable cylindrical lens between slit and grating the image was made stigmatic and the intensity increased so much that strong exposures could be obtained for wavelengths up to about 8500A. For longer wavelengths use was made of a 15 ft. grating with 15,000 lines per inch and a dispersion of about 3.8A per mm. Eastman spectroscopic plates hypersensitized with ammonia were used which gave the best results in each different region.

In the violet and blue the continuous hydrogen spectrum is superimposed on the molecular line spectrum. Very weak lines can therefore not be obtained because they merge with the continuous background, and increasing the exposure time beyond a certain limit would be of no use because it would not bring out new lines but only strengthen the continuous background. We have reached the limit beyond which an increase of the exposure time will not produce any more new lines also for the rest of the spectrum

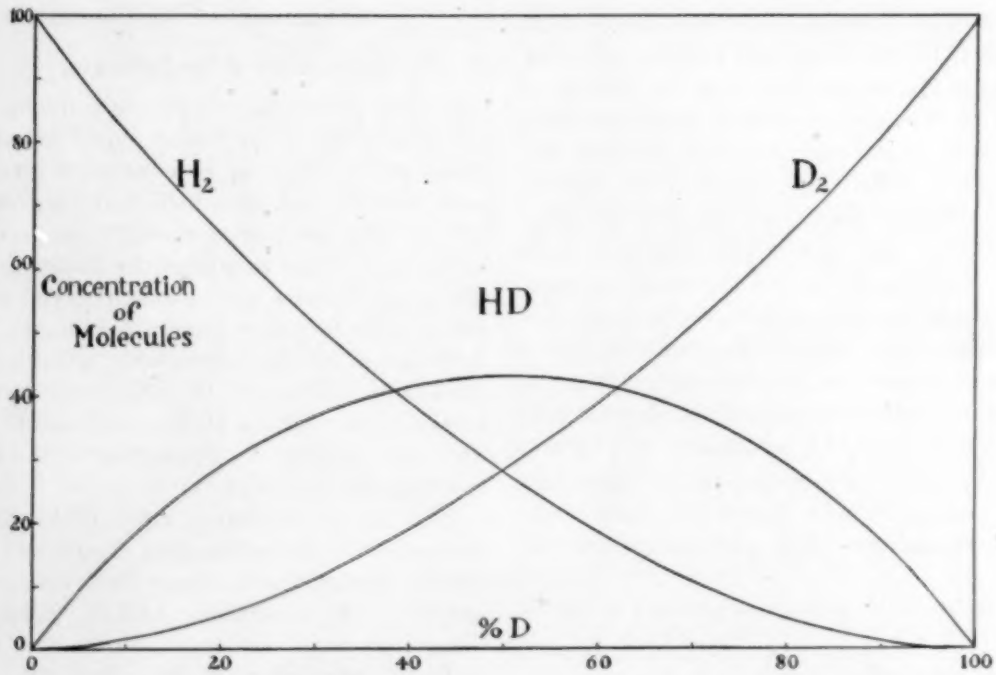

FIG. 1. Concentration of the three types of molecules as function of the deuterium concentration.

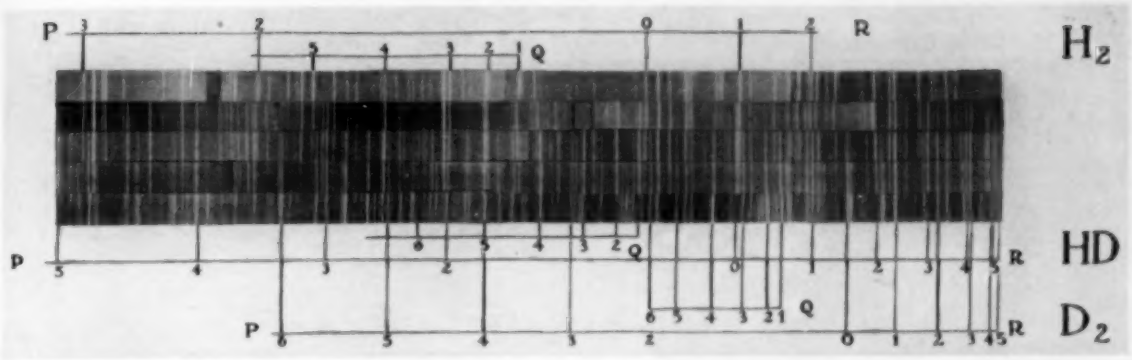

FIG. 2. The 2→2 bands of H_2, HD and D_2. Most of the other lines shown in the figure belong also to the Fulcher bands but are not marked in order to avoid confusion.

except for the longest wavelengths. On the strongest plates the number of lines is so great that neighboring lines begin to flow into each other almost everywhere in the spectrum. As the strong lines are much overexposed on these plates at least one other set is needed with a weaker exposure in order to be able to measure the strong lines. This is necessary for several deuterium concentrations. As the total length of the spectrum is more than 12 feet with our dispersion, we have in this way accumulated several hundred plates which contain many thousand new lines of the hydrogen spectrum.

§3. Measurements

We intend to publish ultimately a complete table of the wavelengths and frequencies of all the lines with their classification, if that is known. Because of the large number of lines to be measured, and because every line should be measured on several plates it will take some time before the complete list is finished. The wavelengths of the present paper are preliminary values, mostly derived from measurements on one plate only, and are possibly subject to slight corrections.

The first task is to ascertain whether a given line is due to H_2, HD or D_2. Theoretically three sets of exposures are sufficient to determine this, one of pure H_2, one of pure D_2 and one of a mixture of approximately equal parts of H and D. This last exposure will show the lines of H_2, HD and D_2 with an intensity ratio of about 1 : 2 : 1. In practice, however, it is advisable to have also exposures at several intermediate concentrations. Fig. 1 shows how the concentrations of the three kinds of molecules depend on the deuterium concentration. If we take photographs of the spectra of mixtures with increasing D concentrations, we find that among the H_2 lines first only HD lines should appear as the D_2 concentration grows only very slowly in the beginning. At higher D concentrations also the D_2 lines appear while the HD lines still increase in strength and the H_2 lines recede. If we get to higher D concentrations than 50 percent the H_2 lines quickly disappear, the HD lines decrease more slowly in strength, whereas the intensity of the D_2 lines still keeps increasing.

It is convenient to mount enlargements of these sets of exposures one below the other (see Fig. 2). A H_2 line will then be strong at the top, diminish in intensity toward the middle and be entirely absent at the bottom. For the D_2 lines just the reverse is true, while the HD lines start fairly well near the top, reach a maximum in the middle and fade out again near the bottom.

In this way it can be easily and surely ascertained to which molecule each line belongs. One advantage of this scheme is that it is easy to recognize blends, which would otherwise not be so easy, unless quantitative intensity measurements were made: e.g., if a line starts at the top but falls off much more slowly than the H_2 lines toward the bottom, it must obviously be a H_2 plus HD blend, whereas if a line starting at the top diminishes in intensity toward the middle but increases again toward the bottom, it must be a H_2 plus D_2 blend. Also, having more than just

TABLE I. *The Fulcher bands of HD.*

J''	*P*-BRANCH ν	*P*-BRANCH I	*Q*-BRANCH ν	*Q*-BRANCH I	*R*-BRANCH ν	*R*-BRANCH I
			1→0			
0	—	—	—	—	18 641.60	8
1	—	—	18 590.89	8	677.11	7
2	18 491.29	2	575.63	8	704.79	5
3	427.48	4	552.87	5	724.44	3
4	357.50	3	522.73	4	735.78	1d
5	281.41	4	485.32	0d		
			2→1			
0	—	—	—	—	18 299.86	9
1	—	—	18 251.46	10	333.35	9
2	18 155.85[1]	8	236.66	10	359.09	7
3	094.38	6	214.54	10	376.66	5
4	026.56	5	185.24	4	385.44	1
5	17 952.50	3	148.96	3		
6	872.03	1	106.02[2]	2d		
			3→2			
0	—	—	—	—	17 969.46	8
1	—	—	17 922.73	10	18 001.97	6
2	17 831.68	5	908.36	10	027.16	7
3	773.31	6	886.90	9	044.57	5
4	708.95	6	858.54[2]	7	053.90[3]	9
5	638.75	1d	823.25	2		
6	562.75	3	781.46	0		
			4→3			
0			—	—		
1			17 604.29	8		
2			590.34	8		
3			569.52	4		
4			541.90	4		
5			507.74	1		
			5→4			
1			17 295.99	1		
2			282.50	1		
			0→0			
0	—	—	—	—	(a)	
1	—	—	16 634.94	7		
2	(a)		623.60	7		
3			606.68	6		
4			584.21	5		
5			556.54	2		
6			523.59	3		
7			485.63	1		
			1→1			
0	—	—	—	—	16 438.78	6
1	—	—	16 390.27	8	476.43	4
2	16 294.91	5d	379.29	8	508.39	6
3	237.52	3	362.88	7	534.36	5
4	175.87	7	341.10	6	554.15	4
5	110.21	6	314.06[2]	5v	567.50	2
6	040.72	3	282.18	3		
7	15 967.71	3	246.35	2		
8	891.40	1				
			2→2			
0	—	—	—	—	16 199.82	7
1	—	—	16 153.53	7	235.40	5
2	16 062.08	5	142.83	7	265.30	3c
3	006.74	6	126.92	7	289.01	4
4	15 947.09	5	105.81	6	305.98	3
5	883.16	4	079.70	5	314.06[3]	(5v)
6	814.80	4	048.62	2		
7	740.73	2				

J''	*P*-BRANCH ν	*P*-BRANCH I	*Q*-BRANCH ν	*Q*-BRANCH I	*R*-BRANCH ν	*R*-BRANCH I
			3→3			
0	—	—	—	—	15 969.43	6
1	—	—	15 924.78	6	16 003.98	5
2	15 837.73	3	914.43	6	033.22	5
3	785.41	5	898.98	5	056.78	4r
4	729.08	8	878.55	4	073.99	3
5	668.78	5	853.27	3	084.59	1
6	604.56	3	823.23	1		
			4→4			
0			—	—		
1			15 704.24	6		
2			694.22	6		
3			679.29	4		
4			659.54	2		
5			635.14	0		
			5→5			
0			—	—		
1			15 492.22	3		
2			482.57	3		
3			468.18	3		
4			449.14	1		
5			425.58	0		
			0→1			
0			—	—	(a)	
1			14 434.29	3		
2	(a)		427.23	4		
3			416.54[2]	(7)		
4			402.62	3		
5			385.32	1		
6			364.79	0		
7			341.26	0		
			1→2			
0	—	—	—	—	14 338.60[4]	10
1	—	—	14 292.31	5	378.47	4
2	14 201.02	2	285.43	9	414.57	5
3	149.83	3	275.19	6	446.73	5
4	096.36	3	261.66	4	474.69	0
5	040.90	3d	244.84	3		
6	13 983.50	1	224.97	2		
7			201.84	0		
			2→3			
0	—	—	—	—	14 199.64	7
1	—	—	14 155.56	8	237.50	10
2	14 068.14[5]	3	148.93	10	271.39	5
3	018.82	3	139.01	5c	301.11	5
4			125.88	5	326.06	3
5	913.16	2	109.72	4	344.42	1
6	856.61	2	090.45	2d		
7			068.14[6]	3c		
8			043.14	0		
			3→4			
0	—	—	—	—	14 067.34	4
1	—	—	14 024.67	9	103.89	5
2	13 941.58	3	018.25	9	137.08	5
3	895.15	3	008.78	10	166.47	7
4	846.65	2	13 996.17	5	191.60	3
5	796.11	2	980.60	3	211.93	2
6	743.32	0	962.05	3		
			4→5			
1			13 900.36	4		
2			894.22	4		
3			885.16	4		
4			873.15	3		
5			858.31	2		
6			840.75	1		

(a) The *P* and *R*-branches of the 0→0 and 0→1 bands show strong perturbations and the classification of several lines is still uncertain. We therefore omit these branches at present.

[1] $+H_2$; [2] $+D_2$; [3] 1→1, Q_3+D_2; [4] 0→1, P_2; [5] Q_7; [6] P_2.

TABLE II. *The Fulcher bands of D_2*

J''	P-BRANCH		Q-BRANCH		R-BRANCH	
	ν	I	ν	I	ν	I
			1→0			
0	—	—	—	—	18 308.38	—
1	—	—	18 274.68	0	332.26	1b
2	18 207.66	0	264.94	3	350.93	1
3	164.68	0	250.36	1	364.09	—
4	117.31	2	231.03	2	369.46	00
5	065.34	0c	207.02	0		
			2→1			
0	—	—	—	—	18 042.39	5
1	—	—	18 009.73	3	065.63	2
2	17 945.11	3	000.24	5	085.05	4
3	903.98	1	17 986.03	3	097.64	1d
4	858.54[1]	(7)	967.12	3	106.02[1]	2d
5	809.32	0	943.71	1		
6	756.01	2	915.75	2		
			3→2			
0	—	—	—	—	17 783.05	4
1	—	—	17 751.60	4	805.27	3
2	17 689.22	3	742.35	5	822.65	4
3	649.26	2	728.46	3	835.07	1
4	605.11	3	710.03	4	842.10	2
5	556.33	2	687.21	2		
6	504.64	3	659.90	2		
			4→3			
0	—	—	—	—	17 530.70	3
1	—	—	17 500.24	2	552.20	3
2	17 440.17	2	491.17	5	569.14	4
3	401.88	4	477.65	3	581.31	1
4	359.36	3	459.67	4c	588.62	4
5	313.02	1	437.34	1	590.72	0
6	262.91	2	410.68	1	586.69	1
			5→4			
1			17 255.45	2		
2			246.62	4		
3			233.41	2		
4			215.88	3		
5			194.05	0		
6			168.14	1		
			6→5			
1			17 017.27	1		
2			008.63	2		
3			16 995.75	1		
4			978.66	1		
5			957.41	0		
6			932.12	0		
			0→0			
0	—	—	—	—	16 695.86	4
1	—	—	16 662.11	3	721.97	2
2	16 595.10	2	654.53	4	744.14	3
3	554.54	2	643.16	5	762.32	2
4	510.57	4	628.09	3		
5	463.55	2	609.37	1		
6			587.09[1]	(5)		
			1→1			
0	—	—	—	—	16 493.42	4
1	—	—	16 460.89	4	18.48	2
2	16 396.22	3	453.49	7	39.51	5
3	356.84	2	442.40	4	56.13	2
4	314.06[1]	5v	427.71	5	66.18	3
5	267.77	4	409.47	2		
6	216.02	4	387.73	2		
7			362.88[1]	(7)		

J''	P-BRANCH		Q-BRANCH		R-BRANCH	
	ν	I	ν	I	ν	I
			2→2			
0	—	—	—	—	16 296.58	4
1	—	—	16 265.06	2	320.97	3
2	16 202.64	2	257.80	6	341.73	3
3	164.94	3	246.98	3	358.65	1
4	124.18	3	232.64	3	371.71	2
5	080.43	2	214.80	2	382.10	1d
6	033.88	2	193.59	2	384.58	1
7	15 984.70	0				
8	932.99	1				
			3→3			
0	—	—	—	—	16 104.82	3
1	—	—	16 074.45	3	128.09	3
2	16 014.27	2	067.41	5	147.67	3
3	15 977.63	3	056.78[1]	4r	163.42	2
4	937.93	3	042.87	3	174.90	2
5	895.17	1	025.36[3]	(7)	180.90	1
6	849.23	2	004.79	1		
			4→4			
0	—	—	—	—	15 918.63	5
1	—	—	15 889.26	3	941.22	4
2	15 831.37	4	882.38	7	960.29	5
3	796.22	4	872.00	4	975.78	3
4	758.19	5	858.49	6	987.43	4
5	717.24	3	841.57	3	994.94	2
6	673.56	4	821.42	4	997.32	2b
7	626.98	2	798.13	1		
8			771.79	2		
9			742.48	0		
10			710.33	0		
			5→5			
0			—	—		
1			15 709.49	2		
2			702.89	4		
3			692.88	3		
4			679.63	3		
5			663.18	2		
6			643.58	2		
7			620.92	0		
8			595.32	0		
			6→6			
1			15 535.59	1		
2			529.09	3		
3			519.39	1		
4			506.52	2		
5			490.54	0		
6			471.53	0		
			0→1			
0	—	—	—	—	14 881.02	5
1	—	—	14 848.32	1	908.13	2v
2	14 783.67	2	843.06	3	932.51	2
3	746.54	1	835.20	2		
4	707.03	0d	824.79	3		
5			811.81	2		
6			796.41	3		
7			778.59	0		
8			758.44	1		

[1] +HD; [2] +H_2; [3] 3→4, R_2; [4] 1→2, P_2; [5] 4→5, R_4; [6] 3→4, Q_2.

TABLE II.—*Continued.*

J''	P-BRANCH		Q-BRANCH		R-BRANCH	
	ν	I	ν	I	ν	I
			1→2			
0	—	—	—	—	14 747.63	5
1	—	—	14 716.22	3	773.79	3
2	14 653.77	3	711.09	6	797.10	6
3	617.81	2	703.39	5	817.09	3
4	579.58	4	693.21	5	831.64	2
5	538.88[3]	5	680.58	4		
6	493.88	5	665.55	4		
7			648.15	2		
8			628.50	2		
9			606.70	0		
			2→3			
0	—	—	—	—	14 618.29	6
1	—	—	14 587.86	4c	643.79	4
2	14 527.75	3	582.84	6c	666.75	5
3	493.34	3	575.38	5	686.99	4
4	456.97	4	565.45	6	704.47	5
5	418.74	3	553.11	4		
6	378.78	4	538.48	4		
7			521.54	2		
8			502.41	2		
9			481.22	1		
10			457.93	1		
			3→4			
0	—	—	—	—	14 492.69	6
1	—	—	14 463.46	4	517.08	4
2	14 405.47	3	458.60	7	538.88[4]	5
3	372.10	2	451.24[3]	8d	557.89	4
4	336.73	4	441.66	6	573.74	4
5	299.40	3	429.69	3		
6	259.94	4	415.50	5d		

J''	P-BRANCH		Q-BRANCH		R-BRANCH	
	ν	I	ν	I	ν	I
			4→5			
0	—	—	—	—	14 372.66	4
1	—	—	14 343.31	4	395.27	3
2	14 289.31	4	338.60[3]	(10)	416.54[1]	(8)
3	255.72	3	331.55	5	435.21	3
4	221.91	5	322.21	7	451.24[3]	8d
5	186.32	2	310.61	3	464.00	1
6	148.93[1]	(10)	296.84	4	472.78	0
7	109.72[1]	(4)	280.95	1		
8			262.98	1		
			5→6			
0			—	—		
1			14 227.88	4		
2			223.33	7		
3			216.52	4		
4			207.49	6		
5			196.30	2		
6			182.98	3		
7			167.62	0		
8			150.29	0		
			6→7			
0			—	—		
1			14 117.56	3		
2			113.19	4		
3			106.64	3		
4			097.98	4		
5			087.24	2		
6			074.47	2		

the necessary three spectra to compare practically eliminates a difficulty, which otherwise would be met, due to the fact that the relative intensities of many lines are very sensitive to changes in the conditions of the discharge tube, as pressure, current and temperature. Only the classification of some very weak lines may remain doubtful.

Good wavelength measurements by Gale, Monk and Lee[4] exist for the H_2 spectrum, and Finkelnburg[5] supplemented their measurements for shorter wavelengths than $H\beta$. For the long wavelength region our plates show many new H_2 lines, especially in the infrared.

The plates taken with moderate deuterium concentrations show the H_2 lines with sufficient intensity so that they can be used as standards for the measurement of the HD and D_2 lines. For those plates which do not show sufficiently strong H_2 lines and in the extreme red and infrared where, due to the lack of interferometrically determined values, Gale, Monk and Lee's measurements are less accurate, iron and neon lines were used as standards. In the infrared the second order of the iron arc had to be used against the first order of the hydrogen lines. In a few limited regions the lack of good standards was provisionally overcome by employing HD and D_2 lines, the wavelength of which could be determined with the help of the combination principle from other known lines. This also served when necessary as a means to identify and eliminate possible small shifts between the hydrogen and the comparison spectrum which are at times difficult to avoid.

§4. The Fulcher bands

As mentioned before, the greatest usefulness for the HD and D_2 spectra will be for the analysis of bands not hitherto found and the interpretation of band systems which presented difficulties until now. It is, however, desirable first to investigate fully a band system which is simple

[4] H. G. Gale, G. S. Monk and K. O. Lee, Astrophys. J. 67, 89 (1928).
[5] W. Finkelnburg, Zeits. f. Physik 52, 27 (1929).

TABLE III. *HD*.

	$R(J-1)-P(J+1)$								
J	1→0	2→1	1→1	3→2	2→2	1→2	3→3	2→3	3→4
1	150.29	144.01*	143.87	137.78	137.74	137.58*	131.70	131.50*	125.76
2	249.63	238.97	238.91	228.66	228.66	228.64	218.57	218.68	208.74
3	347.29	332.53	332.52	318.21	318.21	318.21	304.24		290.43
4	443.03	424.16	425.15	405.82	405.85	405.83	388.00	307.95	370.36
5		513.41	513.43	491.15*	491.18	491.19	469.43	469.45	448.28
	$Q(J)-P(J)$								
J	1→0	1→1	1→2	2→1	2→2	2→3	3→2	3→3	3→4
2	84.34	84.38	84.41	80.81	80.75	80.79*	76.68	76.70	76.67
3	125.39	125.36	125.36	120.16	120.18	120.19	113.59	113.57	113.63
4	165.23	165.23	165.30	158.68	158.72		149.59*	149.47	149.52
5	203.91	203.85	203.94	196.46	196.54	196.56	184.50	184.49	184.49
6		241.46	241.47	234.02*	233.82	233.84	218.71	218.67	218.73
	$R(J)-Q(J)$								
1	86.22	86.16	86.16	81.89	81.87	81.94	79.24	79.20	79.22
2	129.16	129.10	129.14	122.43	122.47	122.46	118.80	118.79	118.83
3	171.57	171.48	171.54	162.12	162.09	162.10	157.67	157.80	157.69
4	213.05	213.05	213.03	200.20	200.17	200.18	195.36*	195.44	195.45
5		253.44*			234.36*	234.70		231.32	231.34

TABLE IV. D_2.

	$R(J-1)-P(J+1)$													
J	1→0	0→0	2→1	1→1	0→1	3→2	2→2	1→2	4→3	3→3	2→3	4→4	3→4	4→5
1	100.72	100.76	97.28	97.20	97.35	93.87	93.94	93.86	90.53	90.55	90.54	87.26	87.22	83.35
2	167.58	167.43	161.65	161.64	101.59	156.01	156.03	155.98	150.32	150.46	150.45	145.00	144.98	139.55
3	233.62	233.57	225.51*	225.45*	225.48	217.55	217.55	217.52	209.78	209.74	209.78	202.10	202.13*	194.63*
4	(298.75)	298.77	288.32	288.36		278.24	278.22	278.21*	268.29	268.25	268.25	258.54	258.49	248.89
6			350.01*	350.16		337.46	337.83	337.76	325.71	325.67	325.69	313.87	313.80	302.31*
							397.40					267.96		354.28
							451.59							
	$Q(J)-P(J)$													
J	0→0	0→1	1→0	1→1	1→2	2→1	2→2	2→3	3→2	3→3	3→4	4→3	4→4	4→5
2	59.43	59.39	57.28	57.27	57.32	55.13	55.16	55.09	53.13	53.16	53.13	51.00	51.01	50.98
3	88.62	88.66	85.68	85.56	85.58	82.05	82.04	82.04	79.20	79.15*	79.14	75.77	75.78	75.83
4	117.52	117.76	113.72	113.65*	113.63	108.58*	108.46	108.48	104.92	104.94	104.93*	100.31	100.30	100.30
5	145.82		141.68	141.70	141.70*	134.39	134.37	134.37	130.38	130.19*	130.29	124.32	124.31	124.29
6				171.71	171.67	159.74	159.71	159.70	155.38*	155.56	155.56	147.77	147.84	147.91*
													171.13	171.23*
	$R(J)-Q(J)$													
1	59.88	59.81	57.58	57.59	57.57	55.90	55.91	55.93	53.67	53.64	53.62	51.96	51.96	51.96
2	89.61	89.45	85.99	86.02	86.01	83.81	83.93	83.91	80.30	80.26	80.28*	77.97	77.91	77.94*
3	119.16			113.73	113.70	111.61	111.67	111.61	106.61	106.64	106.65*	103.66	103.78	103.66
4			138.43	138.47	138.43	138.90*	139.07	139.02	132.07	132.03	132.08	128.95	128.94	129.03*
5							167.30					153.38	153.37	153.39
6							190.99					176.01	175.90	175.94

in structure, and the interpretation of which presents no difficulties. The obvious choice for such a system is the Fulcher bands, as they are free from the complicated effects of the L-decoupling which makes an accurate determination of the band constants practically impossible. Besides, some of the strongest bands of the spectrum belong to this system. The rest of this paper is therefore concerned with a comparison of the Fulcher bands of H_2, HD and D_2.

The data for H_2 are given by Richardson and Das.[6] The Fulcher bands of HD and D_2 are

[6] O. W. Richardson and Das, Proc. Roy. Soc. **A122**, 688 (1929). All the material of these and the other hydrogen

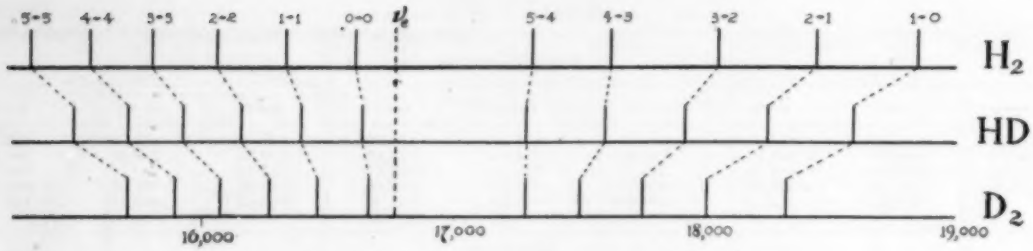

FIG. 3. The Fulcher bands between Hβ and Hα.

presented in the Tables I and II. The intensities are rough estimates only, and the comparison of the intensities of widely separated bands has no meaning as the relative photographic intensities of such bands are chiefly determined by the sensitization of the plate. Recognized blends are designated in the footnotes.

The Tables III and IV give the combination relations for the rotational differences, and can be considered as proof for the correctness of the classification of the lines.

An idea of the appearance of the bands can be obtained from Fig. 2 in which a typical part of the spectrum is reproduced. The top photograph is H_2. The deuterium concentration increases toward the bottom and is about 95 percent in the lowest picture.

Fig. 3 gives a diagram of the position of the bands in the spectrum, whereas Fig. 4 represents the change in the appearance of an individual band. As for H_2, also for HD and D_2 the Fulcher bands form the most conspicuous feature in the green and orange and red, and most of the strong lines in those parts of the spectrum belong to them. Their structure is the same in all three cases with the changes illustrated in Figs. 3 and 4, which originate in the different masses of the molecules. There are other less obvious changes which will be discussed briefly in the last section of this paper.

A very conspicuous feature of the three spectra is the behavior of the intensity alternations. Due to a spin of 1/2, successive rotational lines of the H_2 bands are alternately strong and weak, and the intensity ratio of the strong and weak lines is 3 : 1. Such intensity alternations occur only if the two nuclei of the molecule are identical, and as that is not the case for HD no such alternations must be expected and none are found. In D_2, however, the two nuclei are again identical and accordingly intensity alternations are found. This can be seen easily on Fig. 2, and this figure shows also that the lines with an even number are the strong ones for D_2, whereas for H_2 they were the weak ones. This was found first by Lewis and Ashley,[7] and Murphy and Johnston[8] made quantitative intensity measurements and found that the spin of the D nucleus must have the magnitude 1.

The bands in question are $^3\Pi \rightarrow {}^3\Sigma$ (or more fully $1s\sigma \cdot 3p\pi\ {}^3\Pi \rightarrow 1s\sigma \cdot 2s\sigma\ {}^3\Sigma$) transitions. The triplet separation is, however, negligible, so that the structure of the bands has the appearance of that of $^1\Pi \rightarrow {}^1\Sigma$ bands. This is equally true for all three molecules.

§5. Calculation of the constants

The customary expression

$$F(J) = E_{r/h} = B_v[J(J+1) - \Lambda^2] - D_v J^2(J+1)^2 + \cdots \quad (1)$$

for the rotational energy forms the basis for the calculation of the rotational constants. The formula represents the first terms of a development with respect to powers of $BJ(J+1)/\omega$. For the hydrogen molecule, because of the exceptionally large value of B this quantity is so large that (1) converges very poorly except for the smallest values of J, and for an accurate representation of the rotational energy more terms should be taken into account. This would unduly complicate the evaluation of the con-

bands is given also in O. W. Richardson's book, *Molecular Hydrogen and its Spectrum*, Yale University Press, 1934.

[7] G. N. Lewis and M. F. Ashley, Phys. Rev. **43**, 837 (1933).

[8] G. M. Murphy and H. Johnston, Phys. Rev. **46**, 95 (1934).

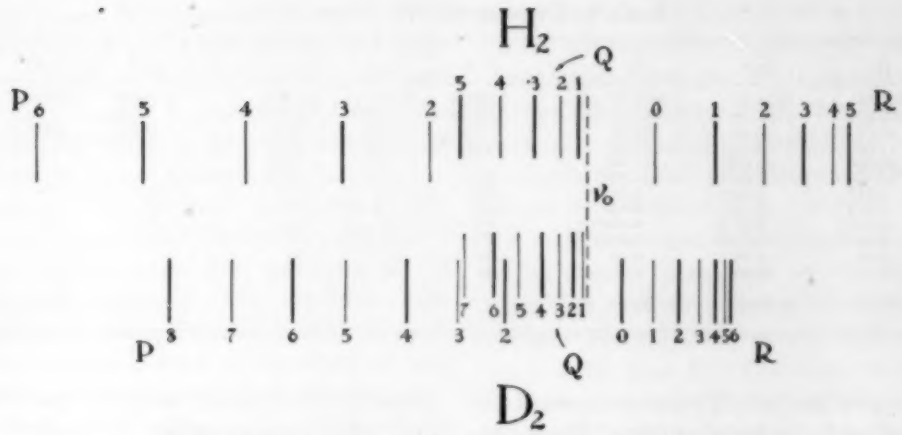

FIG. 4. The change in rotational structure of a typical band.

stants, for it increases the number of constants to be determined empirically. It is true that some of the constants can be expressed in terms of the others and the constants of the vibrational energy. But if one wants to make use of these interrelations in the correct form, the process of evaluating the constants becomes exceedingly tedious. Besides it is hardly certain that at the present stage such a procedure would be of any benefit, for the slight corrections in the wavelengths of some of the lines which the final measurements probably will show will produce changes in the constants of the same order of magnitude as the changes which would result if instead of (1) the more elaborate formula with all refinements were used.

We intend to recalculate the constants making use of all refinements in the final stage of the work, but are confident that this will entail only very minor corrections to the values given in the present paper.

For HD and D_2 the following procedure was adopted. The differences

$$F''(J+1)-F''(J-1)=2(2J+1)B_v''-D_v''[(2J+1)^3+3(2J+1)]+\cdots \quad (2)$$

of Tables III and IV are most conveniently taken to calculate B_v'' and D_v'' of the final $^1\Sigma$ level.[9] With the help of the relation

$$B_v=B_e-\alpha v+\beta v^2-\cdots \qquad (v=0.5,\ 1.5,\ \cdots) \quad (3)$$

the values of B_e and α are found. The most obvious way to calculate the constants of the initial level would be to use the expression analogous to (2). This cannot be done, however, as the $^1\Pi_d$ state which gives rise to the P and R-branches shows many irregularities. The $^1\Pi_e$ state, however, which is the upper level of the Q-branches is regular throughout. The Q-branches are given by

$$Q(J)=A_{v',v''}-B_{v'}-(B_{v''}-B_{v'})J(J+1)+(D''-D')J^2(J+1)^2 \quad (4)$$

and from the frequencies of the Q-lines the constants $A_{v',v''}-B_{v'}$, $B_{v''}-B_{v'}$ and $D''-D'$ can be found. As $B_{v''}$ and D'' are known, the values for $A_{v',v''}$ the origin of the band, $B_{v'}$ and D' can be now determined.

When all the band origins $A_{v',v''}$ are known, the constants in the expression for the vibrational energy

$$E_{v/h}=\omega v-xv^2+yv^3-zv^4+\cdots \qquad (v=0.5,\ 1.5,\ \cdots) \quad (5)$$

can be calculated. For simplicity as many bands (nine in our case) were used as were necessary for a direct computation of the constants.

The rotational constants for the $2s\sigma\ ^1\Sigma$ state of H_2 were calculated by Richardson and Das, and we used their values. These authors failed,

[9] In most cases a least square method was used and the term in $J^2(J+1)^2$ was taken into consideration. The constants given here are the same as those reported in *Nature*. Not all the bands of the Tables I and II were used for their compilation, as some were not yet available at that time.

TABLE V. *The constants of the Fulcher bands.*

	1 H_2	2 HD	3 D_2	2 : 1	3 : 1	3 : 2	ρ_{12}^n	ρ_{13}^n	ρ_{23}^n	n
ω'	2371.58	2054.59	1678.22	0.86634	0.70764	0.81682	0.86616	0.70744	0.81675	1
ω''	2664.83	2308.44	1885.84	.86626	.70768	.81693				
x'	66.27	49.74	32.94	.7506	.4970	.6622	.7502	.5005	.6671	2
x''	71.65	53.77	35.96	.7505	.5018	.6687				
B'	30.364	22.810	15.200	.7512	.5006	.6664				
B''	34.216	25.685	17.109	.7507	.5000	.6661				
α'	1.545	1.020	0.5520	.660	.357	.541	.650	.354	.544	3
α''	1.671	1.099	0.606	.658	.363	.551				
D'	0.0191	0.0116	0.0049	.61	.26	.42	.563	.250	.445	4
D''	0.0216	0.0128	0.0055	.59	.25	.43				
y'	0.88	0.58	0.24	.66	.27	.41				
y''	0.92	0.60	0.34	.65	.36	.57				
ν_0	16793.87	16788.86	16783.92							

however, to give the rotational constants of the $3p\pi\ ^3\Pi_e$ level and the band origins. These constants and the vibrational constants were therefore determined by us in essentially the same way as those for HD and D_2, except that only the three first lines of the Q-branches were used. For these lines the higher terms in (1) are of little importance, and therefore the disadvantage of accidental errors making themselves felt more strongly is compensated by the advantage that systematic errors are less likely to have an influence.

The constants of the three molecules found in the manner indicated above are given in Table V.[10]

COMPARISON OF THE THREE MOLECULES

If we call μ_1, μ_2 and μ_3, respectively, the reduced masses of H_2, HD and D_2, and put $\rho_{ij}=\mu_j/\mu_i$, then every constant occurring in the expressions (1), (3) and (5) for the rotational and vibrational energy, e.g., of HD can be obtained by multiplying the corresponding constant of H_2 by a certain power of ρ_{12}. For this it is essential that it be assumed that the internuclear distance and the forces which hold the molecule together are identical for the two isotopic molecules.

The exponent of ρ_{ij} is: one for ω, two for B_e and x, three for α and y, four for D_e.

Table V shows how accurately these relations are fulfilled by the actual empirical constants of the three molecules. The columns 1 : 2, 1 : 3 and 2 : 3 give the ratios of the respective empirical constants, whereas the columns ρ_{ij}^n give the corresponding theoretical values to which they should be equal.

The theoretical values of ρ_{ij} given in the table were calculated with Bainbridge's values 1.007775 for the mass of the proton and 2.01363 for the mass of the deuton. The contribution of the two electrons to the moment of inertia is *not* taken into account.

An inspection of the table reveals at first sight that all the constants vary with the proper power of ρ_{ij}, but that there are deviations of the observed ratios from their theoretical values which seem to be outside the range of the errors of measurements.

There are three independent causes which may be responsible for these discrepancies. In discussing them let us take the vibrational frequency ω as an example as it is the constant which can be determined with the greatest numerical accuracy.

(A) If we compare the electronic motion of the three isotopic molecules, we would find it exactly the same if the nuclei were kept at rest, as the electronic motion, and therefore also the equilibrium distance and the form of the potential curve would be determined then completely by the charges of the nuclei which are the same in all cases. Of course an actual molecule with the nuclei at rest does not exist. We have to extrapolate to the vibrationless and rotationless molecule. This we do with the help of the formulae (1) to (5). But this is not actually the same as if we took a molecule with fixed nuclei, which becomes apparent from Kronig's treatment of the problem.[11]

[10] This table is calculated from the same material as the table given in *Nature* (reference 1). The changes are due to a numerical error (omission of the term with Λ^2) in the previous calculations.

[11] R. de L. Kronig, Physica **1**, 617 (1934).

Both the internuclear distance and the form of the potential curve which determines the value of ω may be slightly different for the different isotopes, but the exact magnitude of this deviation can only be found, if the wave functions of the electronic state are known.

(B) Even if the potential curve were completely known, there would be still an uncertainty in the relations between the constants of the three isotopic molecules. The electrons contribute to the moment of inertia and the magnitude of this contribution is not known, as long as the electronic wave functions are not sufficiently known. The values of ρ_{ij} given in the table, calculated without taking the mass of the electrons into account, are certainly not the correct ones for our case as it is certain especially as the levels are excited ones that $\psi\bar{\psi}$ is different from zero for a considerable distance from the axis of rotation. Perhaps a better approximation is to take the electrons as coinciding with the nuclei. In that case we obtain

$$\rho_{12}=0.86620 \qquad \rho_{13}=0.70754 \qquad \rho_{23}=0.81683.$$

These values are a little closer to the observed ones, but this can hardly be taken as justification for this assumption, as long as we are not certain of the contribution of the other causes.

(C) The third possible cause for the discrepancies is of a different nature from the two previous ones. In calculating ω use is made of (5) which is only an approximation. Neglecting the higher terms causes systematic errors in the values of the constants which though slight are of sufficient magnitude to account for the discrepancies. That a considerable part of the discrepancies is probably due to this cause is made probable by the fact that if the fourth power term in (5) is neglected, the discrepancies become much larger and of the opposite sign. The same causes can also be held responsible for the deviations of the other constants, but as their accuracy (except for ν_0) is less, practically only the third cause will be of any importance.

There may be a considerable error in the value of B_e if there is any L decoupling. This produces an additional term in $J(J+1)$ which unless it can be determined separately, gives a wrong value for the equilibrium distance and also wrong values for the ratios. For the two levels under consideration this effect is, however, absent as the lower level is a $s\sigma\Sigma$-term[12] which has no L decoupling and the upper level is a $p\pi\Pi$ term. One of the components of such a level does not show any effects of L decoupling and it is very probable that our $p\pi\Pi_c$ level for which the constants were calculated is this level.

Finally we come to the origins of the systems, which should correspond to the pure electronic transition. We find that the origin of the HD system lies almost exactly halfway between that of H_2 and D_2. The separation of 5 cm^{-1} between H_2 and HD and HD and D_2 is unquestionably real and cannot be produced wholly by experimental errors. It must be attributed to the kind of interactions mentioned under (A). It may be noted that the separation is of the opposite sign as the separation between Hα and

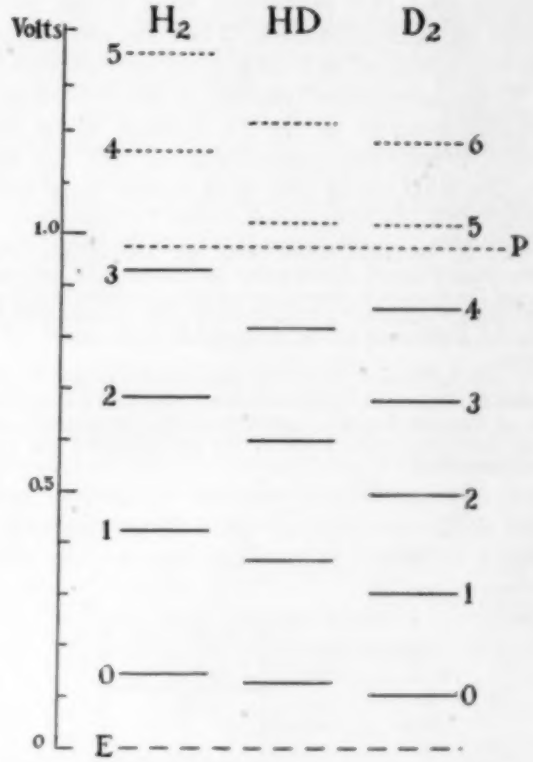

FIG. 5. The vibrational levels of the $3p\pi\ ^3\Pi$ state. Those above P have their Π_d component predissociated.

[12] The designation $s\sigma$ etc. refers to the second electron. The first electron is in all levels under consideration $1s\sigma$ and can be omitted for convenience from the term symbols without giving rise to ambiguities.

$D\alpha$. It is clear that the cause of this latter separation, namely that the nucleus moves about the common center of gravity of nucleus and electron plays a very much smaller part if two electrons are present, which are on opposite sides of the nucleus.

The isotopic separation of the origins of the Fulcher bands is of the same order of magnitude as the separation of the origins of the far ultraviolet bands.[13]

Perturbations

There are irregularities in the rotational levels of the $3p\ ^3\Pi_d$ state in all three molecules which result in irregularities in the P and R-branches. We shall postpone a discussion of the details of these perturbations until a later paper as for their complete understanding a knowledge of the perturbing level is necessary. It is practically certain that this perturbing level is the level called by Richardson $3p\sigma\ ^3\Sigma$ but the analysis of the bands originating from it is not yet complete.[14]

Richardson noticed that the R and P-branches are absent for all of the H_2 Fulcher bands for which $V' \geq 4$. The same is true for HD, but for D_2 the $4 \rightarrow 3$, $4 \rightarrow 4$ and $4 \rightarrow 5$ bands show well developed P and R-branches while they are absent for $V' \geq 5$. The explanation for this behavior must be that those vibrational states of the $3p\pi\ ^3\Pi_d$ level which are not observed interact with a dissociated level which cannot interact with the Π_e level. (A $p\sigma\ ^3\Sigma$ level would be such a level.) If this is the case we have a method to determine the heat of dissociation of hydrogen independent of any of the other methods used for H_2 before.

Fig. 5 shows the vibrational levels of the $3p\pi\ ^3\Pi$ states. Those for which $^3\Pi_d$ is predissociated are represented by broken lines. The limit of dissociation which is with sufficient approximation the same for the three molecules must lie between the highest complete level which is $V=3$ of H_2 and the lowest predissociated one which is $V=5$ of D_2.

These two levels lie 0.78 and 0.87 volt above the lowest vibrational level of the $3p\pi\ ^3\Pi$ state of H_2. This level, according to Richardson is 13.80 volts above the ground level of the molecule. Therefore the two limiting levels have a total energy of 14.58 and 14.67 volts, respectively. The products of dissociation are evidently a normal atom and an excited one with 10.15 volts of energy. The heat of dissociation of the normal molecule must lie therefore between 4.43 and 4.52 volts. This agrees excellently with the value 4.465 volts determined by other means.

It is a pleasure to thank Professor H. S. Taylor of Princeton for the heavy hydrogen which made this investigation possible, and we are indebted to Dr. C. R. Jeppesen who carried out some of the measurements.

[13] C. R. Jeppesen, Phys. Rev. **45**, 480 (1934). The separation is given in the paper as 135 cm^{-1}. This large value, Dr. Jeppesen informs us is due to a numerical error. The correct value is 9 ± 5 cm^{-1} which is in agreement with the value obtained by K. Mie (Zeits. f. Physik **91**, 475 (1934)).

[14] *Note added with proof.* The analysis of the perturbing bands has been completed in the meantime and will appear in the *Physical Review*. It confirms all the statements made here concerning the nature of the perturbations and the predissociation.

Transmutations of Nitrogen by Deutons

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Nitrogen bombarded by deutons emits three alpha-particle and two proton groups. For deutons of maximum energy 1.4 mv traversing an air target the alpha-particle groups have ranges of 6.9, 7.8 and 12.7 cm. The reaction involved is $N^{14}+D^2 \rightarrow C^{12}+He^4$, and the transmutation energy, derived from the long range group, in conjunction with the precise mass spectrograph determinations of D^2, He^4 and C^{12} yields for the mass of N^{14} the value 14.0069. The 6.9 and 7.8 cm groups indicate the existence of excited levels in C^{13} at 3.8 and 4.7 mv. The proton groups from a thin air target bombarded by 1.25 mv deutons have ranges of 24 and 85 cm. The reaction involved is $N^{14}+D^2 \rightarrow N^{15}+H^1$. The transmutation energy of this reaction yields for the mass of N^{15} the value 15.0041. The 24 cm group indicates an excitation level in N^{15} at 4.7 mv. For 1.2 mv deutons, the effective nuclear collision cross sections for the alpha-particle and proton reactions are about 10^{-27} cm^2 and 3×10^{-29} cm^2, respectively.

INTRODUCTION

IN experiments in our laboratory,[1] which were in the nature of a preliminary survey of nuclear reactions induced by deutons and protons, there was noted a particularly strong emission of alpha-particles of about 6.8 cm range from a target of NH_4NO_3 bombarded by 1.2 mv deutons. The absence of this alpha-particle group from other targets containing oxygen indicated that nitrogen was the element involved in the reaction. In those early experiments the emission of protons and neutrons from the nitrogen target was also observed.[2] Meanwhile Livingston and McMillan[3] have found that radio-oxygen is formed when nitrogen is bombarded by deutons, the reaction involved being the one in which neutrons are emitted.

We have lately carried out a more detailed investigation of the reactions of deutons with nitrogen, which confirms and extends the earlier observations, and this is the subject of the present paper.

APPARATUS

In these experiments a beam of 2.2 mv deutons was brought out from the larger of our instruments for the acceleration of ions through an aluminum window (1 cm stopping power) into the air. The air itself provided a convenient nitrogen target. Observation of the blue glow produced by the deuton beam in the air furnished immediate and reliable evidence of the homogeneity and range of the deutons.

In Fig. 1 is shown the arrangement of slits for defining the deuton beam and collimating the emitted particles from a thin target of air. The arrangement is ideal in two respects. The use of an essentially thin target made it possible to resolve proton or alpha-particle groups near in range, and the possibility of contaminations from the walls or target support is not present. All observed radiations excepting the neutrons and gamma-rays necessarily come from the air, as the beam nowhere impinges on anything but air within sight of the recording ionization chamber. The radiations were recorded as usual with a shallow ionization chamber (4 mm deep) and a linear amplifier, in conjunction with a cathode-ray oscillograph and Wynn-Williams thyratron recording mechanism. Visual observations with the cathode-ray oscillograph provided a con-

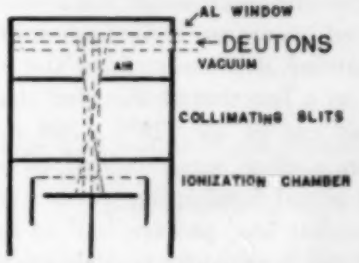

FIG. 1. Arrangement of slits defining the gas target and the beam of disintegration particles recorded by the Wynn-Williams ionization chamber.

[1] G. N. Lewis, M. S. Livingston and E. O. Lawrence, Phys. Rev. **44**, 55 (1933).
[2] E. O. Lawrence and M. S. Livingston, Phys. Rev. **45**, 220 (1934).
[3] M. S. Livingston and E. McMillan, Phys. Rev. **46**, 437 (1934).

tinuous indication of the nature of the ionizing particles recorded, while by altering the bias on the thyratrons, the protons could be distinguished from the alpha-particles.

Alpha-Particles

For the observation of the alpha-particles 12 mm slits 3 cm apart were used, the first slit being one cm from the deuton beam. The air target thus had an effective thickness of about 1.5 cm, and since the deutons traversed 1.5 cm of air after passing through this region, the effective energy of the bombarding deutons varied from 1.4 mv to 0.85 mv across the target. With a high bias on the thyratrons, only alpha-particles and heavy neutron recoil nuclei were recorded. The bias used in these experiments for the alpha-particle observations was about three times that used for the proton measurements. By visual observations with the cathode-ray oscillograph it was quite easy to distinguish the alpha-particles from the neutron recoils because the alpha-particles gave ionization pulses of more or less constant amounts, while the recoil nuclei gave pulses over a wide range of values, larger and smaller.

The ranges of the particles were determined in the usual way by placing absorbers between the ionization chamber and the target. This was accomplished both by simply moving the chamber back from the slits and using the air itself as an absorber, and by interposing 0.001 inch aluminum foils. Calibration of the foils in previous experiments using the alpha-particles from lithium showed that 0.001 inch aluminum has a stopping power of almost exactly 4 cm of air.

The alpha-particle observations are shown in Fig. 2. The ordinates record the actual number of observed counts per second per microampere of bombarding deutons striking the aluminum window, as a function of absorber thickness in equivalent cm of air (20°C, 760 mm). The aluminum window was mounted on a grid so that the actual bombarding current in the air was somewhat less, perhaps half as much. Because of the large alpha-particle emission, the bombarding currents used were only a few hundredths of a microampere. For absorbers less

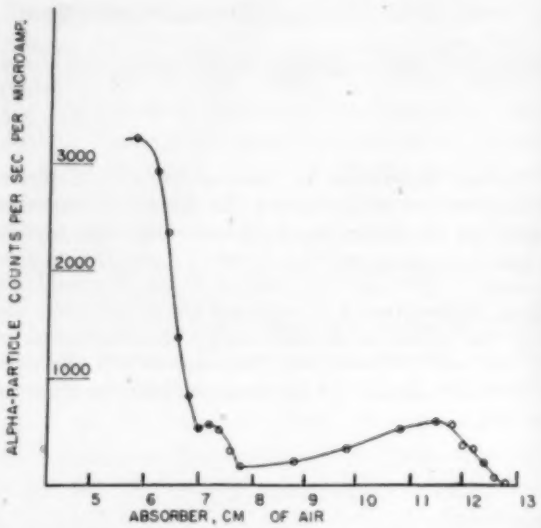

Fig. 2. Range distribution of alpha-particles from a 15 mm thickness of air bombarded by 1.4 mv deutons.

than 12.5 cm, the alpha-particle counts greatly outnumbered those produced by neutron recoils, and the data in Fig. 2 may be regarded as entirely due to the former.

It is seen that there are three alpha-particle groups of ranges 12.7 cm (11.2 mv), 7.8 cm (8.3 mv) and 6.9 cm (7.7 mv). We made observations in the region below 5.5 cm, and obtained evidence of another alpha-particle group of shorter range, but we wish to examine this region more closely before presenting any evidence.

The shortest range group, which is by far the most intense, agrees with our earlier preliminary observations[1] using an NH_4NO_3 target. However, to make more certain that all three alpha-particle groups are due to the reaction of the deutons with nitrogen, the alpha-particle observations were repeated with the air replaced by oxygen. The alpha-particle counts with oxygen were less than 1 percent of those from the air and those that were obtained were evidently neutron recoils.[4] Thus the alpha-particles observed are to be ascribed to nitrogen.

[4] With illuminating gas, rather than oxygen in place of the air, we obtained a very large number of counts, more than from the air itself. In this case also visual observations with the cathode-ray oscillograph showed that the ionization pulses were due to neutron recoil nuclei in the ionization chamber, indicating a copious emission of neutrons from a constituent of the illuminating gas, which was

The reaction here involved doubtless is

$$N^{14}+D^2 \rightarrow C^{12}+He^4.$$

The longest range group of alpha-particles almost certainly corresponds to the case where the entire energy released in the reaction is in the form of kinetic energy of the alpha-particle and the recoil carbon nucleus. The energy released in the transmutation, called henceforth the transmutation energy, is readily calculated from the observed energy of the long range alpha-particles, taking account of the maximum energy of the deutons, 1.4 mv, and momentum considerations involved in the recoil of the carbon nucleus. Thus it is calculated that the transmutation energy is 13.7 mv, corresponding to a loss of mass in the reaction of 0.0147 mass units. All of the masses involved in this reaction have been measured with the mass spectrograph. Because D^2, He^4 and C^{12} have all been measured with great precision, greater than that of N^{14}, this datum may be used for an evaluation of the mass of N^{14} of comparable precision, thus,

$$\begin{aligned} N^{14} &= C^{12}+He^4-D^2+(\text{transmutation energy}) \\ &= 12.0036+4.0022-2.0136+0.0147 \\ &= 14.0069. \end{aligned}$$

This value agrees satisfactorily with that of Aston,[5] 14.008, and Bainbridge's[6] later determination, 14.0074.

The 6.9 and 7.8 cm alpha-particle groups presumably are emitted with the C^{12} nucleus (or the alpha-particle) left in an excited state in each case. The total kinetic energy of the alpha-particles and the recoil nuclei in excess of the kinetic energy of the bombarding deuton is calculated to be 9.0 and 9.9 mv for the two groups. Thus it appears that there are two gamma-ray levels in C^{12}, one of 3.8 mv and another of 4.7 mv, though of course the possibility that one (or both) of the levels belongs to the alpha-particle cannot be excluded.

Although we have some evidence that gamma-rays are emitted from a nitrogen target under deuton bombardment, we have not examined the question carefully as yet, and have not established that these gamma-rays have energies corresponding to these alpha-particle groups. There is, however, independent evidence of these excitation levels. Bothe and Becker[7] have observed by means of coincidence Geiger counters the emission of a 5 mv gamma-ray from beryllium bombarded by alpha-particles. This gamma-ray presumably comes from excited C^{12} formed with the emission of a neutron. Crane and Lauritsen[8] have observed the gamma-rays from boron bombarded by deutons. By measuring the curvature of electron and positron tracks produced by the gamma-rays in a Wilson chamber placed in a magnetic field, they have obtained evidence for at least four gamma-rays of 2.4, 4.2, 5.6 and 6.7 mv energy. Crane, Delsasso, Fowler and Lauritsen have identified their 5.6 mv gamma-ray with the 5 mv gamma-ray of Bothe and Becker, both being ascribed to the same excitation level of C^{12}. It is possible that the 4.7 mv energy derived from the present data represents another measure of the same energy level.

On the assumption that the alpha-particle emission is isotropic, it is readily calculated from the data of Fig. 2, taking account of the geometry of the slit system, that about one alpha-particle was emitted from the 15 mm thickness of air for every 10^7 deutons, having an average energy crossing the air target of 1.15 mv. Taking account of the number of nitrogen atoms in this thickness of air, this transmutation yield may be expressed in terms of an effective cross section for transmutation, which is 10^{-27} cm^2, or a corresponding effective radius of about 2×10^{-14} cm. This value is small compared to the nuclear radius deduced from scattering experiments. In other words, the chance of transmutation in a close collision is small.

Protons

The range distribution of the protons emitted from the air target is shown in Fig. 3. Here the bias in the thyratron counter is such that only

doubtless carbon. That carbon emits neutrons under deuton bombardment was shown in our first experiments with deutons (M. S. Livingston, M. C. Henderson and E. O. Lawrence, Phys. Rev. **44**, 781 (1933)), and more recently it has been established that these neutrons are emitted in the reaction in which radio-nitrogen is formed.

[5] F. W. Aston, Proc. Roy. Soc. **A115**, 503 (1927).

[6] Unpublished. We wish to thank Dr. Bainbridge for communicating to us directly this recent measurement.

[7] W. Bothe and H. Becker, Zeits. f. Physik **76**, 421 (1932).

[8] H. R. Crane, L. A. Delsasso, W. A. Fowler and C. C. Lauritsen, Phys. Rev. **46**, 1109 (1934).

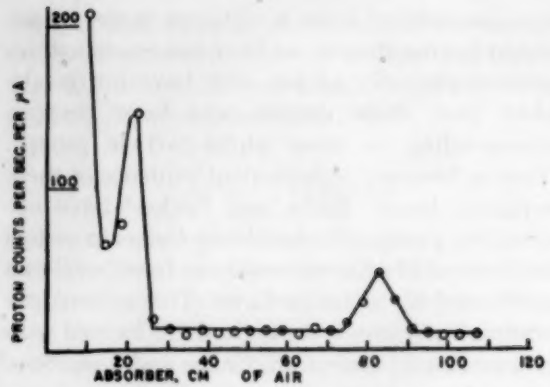

FIG. 3. Range distribution of protons from 15 mm air target bombarded by 1.4 mv deutons.

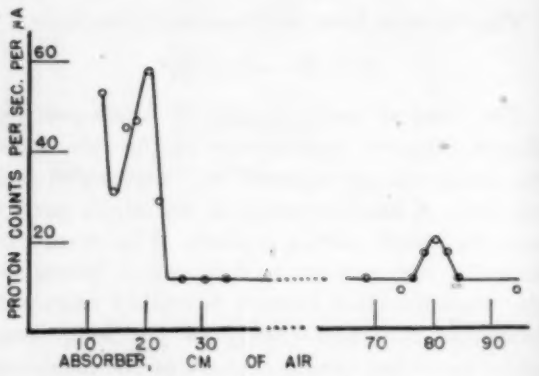

Fig. 4 Range distribution of protons from 5 mm air target bombarded by 1.25 mv deutons.

those protons were counted that were within a few centimeters of the end of their range. Again deutons of energies between 0.85 and 1.4 mv bombarded an air target of 15 mm thickness, the same geometry of slits being used as was employed in the alpha-particle observations. There are two distinct proton groups of ranges 91 and 26 cm. The counts observed at shorter range are due to the alpha-particles. When the air was replaced[9] by oxygen, these two proton groups disappeared. This observation is consistent with those of Cockcroft and Walton,[10] who ascribed to oxygen 4 and 8 cm proton groups, and of Rutherford and Oliphant,[11] who have come to the conclusion that an 8 cm group arises from bombardment of oxygen by deutons. The 91 and 26 cm groups are therefore to be ascribed to nitrogen, and presumably are involved in the reaction

$$N^{14}+D^{2}\rightarrow N^{15}+H^{1}.$$

In order to examine more carefully the homogeneity and range of these two proton groups, the slits defining the width of the air target and the angular divergence of the disintegration protons collected by the ionization chamber were narrowed to 3.5 mm, the slits being as before 3 cm apart, at right angles to the deuton beam. With this very narrow air target and very small spread in solid angle of the disintegration protons arriving at the ionization chamber, and with the thyratron bias voltage such that only those protons that were within 2 cm of their range were recorded, the counts shown in Fig. 4 were obtained. The two proton groups show themselves sharply[12] and distinctly above the uniform background due to the neutrons.[13]

With the narrower slits the energy of the deutons when passing across the thinner air target varied from 1.25 to 1.05 mv. The sharpness of the proton groups was quite consistent with this spread in energies, thus indicating that the groups are homogeneous, to a high degree, with maximum ranges of 24 cm (4.1 mv) and 85 cm (8.5 mv). Again the long range group is doubtless emitted in the reaction in the case when all of the energy released is converted into kinetic energy. The 85 cm protons correspond to a transmutation energy of 8.0 mv (0.0086 mass

[9] With illuminating gas in place of the air, a very large emission of protons was observed, having ranges as great as 90 cm. These long range protons, which are probably emitted in the formation of C^{13}, in which the whole transmutation energy is given to the emitted proton, are being investigated in detail and will be reported later.

[10] J. D. Cockroft and E. T. S. Walton, Proc. Roy. Soc. **A144**, 704 (1934).

[11] Lord Rutherford and M. L. E. Oliphant, mentioned by Cockcroft and Walton, reference 10.

[12] The homogeneous long range group obtained in this way has been found to be very useful in checking the performance of the ionization chamber-linear amplifier combination, that is, in finding out what range of proton energies is counted by the apparatus for any given bias voltage. Later on we hope to use this group in measurements on the Bragg ionization curve for protons, as there seems to be some uncertainty about this matter at the present time.

[13] The neutrons which gave rise to the counts with absorbers between 25 and 75 cm and also beyond 90 cm, were due in part to the nitrogen reaction in which radio-oxygen is formed,[3] and in part to the aluminum and carbon (wax) of the window through which the deuton beam emerged from the vacuum chamber.

units). This datum may be used to evaluate the mass of N^{15} as follows:

$$N^{15}=N^{14}+D^2-H^1-(\text{transmutation energy})$$
$$=14.0069+2.0136-1.0078-0.0086$$
$$=15.0041.$$

This is to be compared with the value derived from band spectra data by Birge and Menzel[14] of 15.0032.

The 24 cm proton group corresponds to a kinetic energy release in the reaction of 3.3 mv, and the obvious interpretation is that when these protons are emitted, N^{15} is left in a 4.7 mv excitation level.

The experimental observations indicate that about a thirtieth as many protons as alpha-particles are emitted from nitrogen. In other words, the effective collision radius for the formation of N^{15} is about 4×10^{-15} cm.

The fact that the alpha-particle emission is considerably greater than the proton emission may be interpreted to indicate that the nuclear barrier (of C^{13}) for alpha-particles is less than the energy with which they are released (8 mv). This is quite in accord with the estimate of 3.6 mv for the nuclear barrier of carbon deduced from scattering experiments, as given by Pollard.[15]

These experiments have been aided by grants from the Research Corporation and the Chemical Foundation.

[14] R. T. Birge and D. H. Menzel, Phys. Rev. **37**, 1669 (1931).

[15] E. W. Pollard, Phil. Mag. **16**, 1131 (1933).

FEBRUARY 15, 1935 PHYSICAL REVIEW VOLUME 47

Note on the Scattering of X-Rays from Fluids Containing Polyatomic Molecules

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(Received December 10, 1934)

The intensity of the (unmodified) scattered radiation from a fluid containing one kind of molecules is given by:

$$S=(1/\Sigma_n Z_n)\left[F_1^2+F_2^2\int P_{(R)}dR(\sin kR)/kR\right],$$

where $F_1^2=\Sigma_n\Sigma_m f_n f_m(\sin kr_{nm})/kr_{nm}$, while F_2^2 depends both upon the molecular structure and upon the relative orientation of the molecules. It is shown that the radial distribution function P_R may be obtained directly from the observed scattering curve if the molecular structure is known:

$$P_{(R)}=4\pi R^2\rho_0+\frac{2R}{\pi}\int_0^\infty k\left[\frac{S\Sigma_n Z_n}{F_1^2}-1\right]\frac{F_1^2}{F_2^2}\sin(kR)dk,$$

where ρ_0 is the density of the fluid in molecules per unit volume.

WHEN x-rays are scattered from a fluid containing only one kind of atoms (strictly speaking we should require the atoms to be equivalent as well), the intensity of the (unmodified) scattered radiation is given by[1]

$$S=(f^2/Z)\left[1+\int 4\pi r^2\rho_0 w_{(r)}dr(\sin kr)/kr\right]. \quad (1)$$

where S is the intensity expressed in terms of the Thomson scattering. Z is the atomic number, f the scattering power of the atom and $k=4\pi\sin\theta/\lambda$. $4\pi r^2\rho_0 w_{(r)}dr$ (where ρ_0 is the density of the fluid in atoms per unit volume) represents the probability of finding an atom at a distance between r and $r+dr$ from any given one. As shown by Zernike and Prins[2] and by Debye and Menke[1], the radial distribution function may be obtained directly from the observed scattering curve, the result being:

[1] P. Debye and H. Menke, Ergebn. d. Techn. Röntgenkunde **2**, 1 (1931); compare also reference 2.

[2] Zernike and Prins, Zeits. f. Physik **41**, 184 (1927).

$w_{(r)}=1+g(r)/4\pi r^2\rho_0$ where

$$g(r)=\frac{2r}{\pi}\int_0^\infty k\left[\frac{ZS}{f^2}-1\right]\sin(kr)dk. \quad (2)$$

Eq. (2) has been used with success in several instances.[1, 3, 4, 5]

The object of this note is to point out that the radial distribution function may be obtained directly also in the case of a fluid containing polyatomic molecules provided that the molecular structure is known.

We will assume that the fluid contains only one kind of molecules and that all orientations of any one molecule are equally probable. We find readily:

$$S=\frac{1}{\sum_n Z_n}\left[F_1^2+F_2^2\int 4\pi R^2\rho_0 W_{(R)}dR\frac{\sin kR}{kR}\right], \quad (3)$$

where Z_n is the number of electrons in the nth atom of the molecule, while $4\pi R^2\rho_0 W_{(R)}dR$ (ρ_0 now being density in molecules per unit volume) represents the probability of finding a molecule at a distance between R and $R+dR$ from any given one. The quantity F_1^2 is the familiar one

$$F_1^2=\sum_n\sum_m f_n f_m(\sin kr_{nm})/kr_{nm}, \quad (4)$$

while F_2^2 in general is different from F_1^2. The expression for F_2^2 depends both upon the molecular structure and upon the relative orientation of the molecules. If we assume that all molecules are parallel at any instant, F_2^2 becomes identical with F_1^2. In the other extreme case when the relative orientation is purely random, we find:

$$F_2^2=[\sum_n f_n(\sin kr_n)/kr_n]^2, \quad (5)$$

where f_n is the scattering power of the nth atom and r_n its distance from the center of the molecule. This latter expression for F_2^2 has been used for the special case of a diatomic molecule by Debye[6] and by Menke[3] for the special case of carbon tetrachloride. If the relative orientation is a restricted random one (as for example when the axes of the various molecules remain parallel), the expression for F_2^2 becomes more complicated. Quite generally, however, F_2^2 will decrease more rapidly with increasing k than F_1^2, so that the intermolecular interference (given by the integral term in Eq. (3)) at large values of k will become of less importance than otherwise might have been expected.

If the molecular structure is known, we may calculate F_1^2 and F_2^2, and Eq. (3) may be solved for the distribution function $W_{(R)}$ by means of the Fourier reciprocity relation.[7] We find readily:

$W_{(R)}=1+G_{(R)}/4\pi R^2\rho_0$ where

$$G_{(R)}=\frac{2R}{\pi}\int_0^\infty k\left[\frac{S\sum_n Z_n}{F_1^2}-1\right]\frac{F_1^2}{F_2^2}\sin(kR)dk. \quad (6)$$

If the symmetry of the molecule is fairly high (and also if the temperature is high), it is to be expected that the relative orientation of the molecules will be practically random, so that Eq. (5) may be used for F_2^2.

It has been customary hitherto to account for the diffraction pattern of fluids by assuming a radial distribution function and then calculate the intensity according to Eq. (3). The calculated and observed scattering curves were then compared. (This is for example the procedure followed by Menke in his paper on liquid CCl_4.)[3] By Eq. (6) a more direct method of attack is made possible.

It is worth while noticing that the integrand in Eq. (6) approaches zero with increasing k (the molecules scatter independently), so that the observations need not extend to extremely high values of k in order to give a reliable radial distribution function. This is, of course, in agreement with the well-known fact that the liquid scattering curve approaches the pure gas scattering curve as the scattering angle increases.

[3] H. Menke, Phys. Zeits. **33**, 597 (1932).
[4] B. E. Warren and N. S. Gingrich, Phys. Rev. **46**, 368 (1934).
[5] B. E. Warren, J. Chem. Phys. **2**, 551 (1934).
[6] P. Debye, Phys. Zeits. **28**, 140 (1927).
[7] Menke's paper (reference 3) contains the statement that one cannot solve for $W_{(R)}$ because F_1^2 and F_2^2 are different. This statement must be due to an oversight.

The Emission of Electrons by Swiftly Moving Mercury Ions

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(Received January 2, 1935)

Various metal targets bombarded by swiftly moving ions emit from 7 to 20 electrons per incident ion. The majority of these secondary electrons have energies less than 10 electron volts. The commonly used metals such as nickel, copper, molybdenum, aluminum, tungsten, silver, tin, magnesium and cadmium differ but little from one another in emission of electrons. The emission is an increasing function of the ionic energy in the range 0.7 to 2.35 mv. Targets of molybdenum and tungsten heated in vacuum have shown a decreased emission but the effect is temporary. Freshly formed films of the alkali metals show a steadily increasing emission for some time after formation. In the case of lithium the effect is extremely rapid and the emission reaches values as high as 50 electrons per incident ion.

ASIDE from its general interest, the emission of electrons by impact of swiftly moving ions is important in the theory of high voltage breakdown, and hence in the design of high voltage vacuum tubes. Previously published work with very energetic particles has always dealt with alpha-rays, and therefore it seems desirable to study the problem with various other energetic ions. Fortunately these fast ions can now be obtained in a number of ways. In the present work mercury ions were accelerated to energies up to 2.35 mv by a method due to Sloan and Lawrence,[1] and extended by Sloan and Coates.[2]

APPARATUS

Singly-charged mercury ions are produced in the plasma of a hot-cathode mercury arc and drawn through a canal tube into the high frequency oscillating system, which accelerates them to a high velocity. The high frequency system is constructed in the following way; alternate members of a series of 36 short coaxial copper cylinders act as a capacity and are connected to opposite ends of a small inductance. The length of the Nth tube is the product $L_1(N)^{\frac{1}{2}}$, where L_1 is the length of the first accelerator; this allows charged particles to be accelerated through the series of tubes in synchronism with the oscillating field and to emerge with 36 times the energy acquired by crossing a single gap. Inasmuch as the capacity is fixed, the synchronizing potential and hence the energy of the ions is varied in practice by changing the value of the inductance. The ionic energy can be determined quite accurately by a kinematical relation between the frequency of oscillation and the geometry of the accelerating system.

Precaution must be taken to keep the collected beam free of x-rays and electrons. Therefore the beam is electrostatically deflected through a small angle and into a collimating tube in which x-rays are absorbed by a series of slitted stops. All x-rays and electrons in the main body of the tube except those following the beam can be stopped by a grounded lead ring at the end of the accelerating system, and those remaining electrons which are with the beam are stopped by electrostatic and magnetic deflection. There will be secondaries formed in the collimating tube wherever the ion beam may strike, but these are slow electrons that can be stopped by a 45 volt retarding potential indicated in Fig. 1.

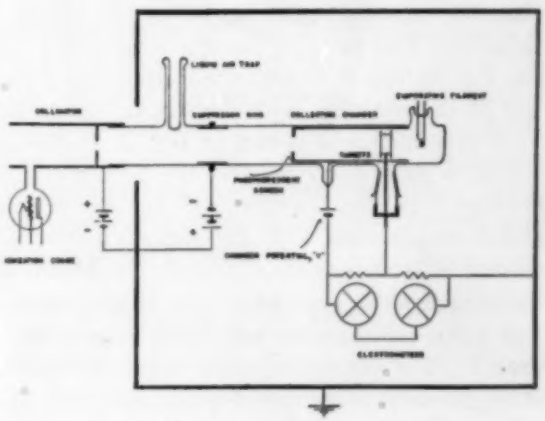

FIG. 1. Collector. (The vertical line representing a lead from the targets should have been drawn on down to join the direct connection between the two electrometers.)

[1] D. H. Sloan and E. O. Lawrence, Phys. Rev. **38**, 2021 (1931).

[2] D. H. Sloan and W. M. Coates, Phys. Rev. **46**, 539 (1934).

The Collector

Proper alignment of the collector is assured by the presence of a phosphorescent screen on the collector front which remains dark only if the beam does not strike it. Two targets are mounted on a ground joint, and fresh films can be evaporated upon them from a metallic pellet heated by a conical filament. Variations of the apparatus have included distilling tubes for the generation of alkali metal films, and a filament and circuit to heat a single target of a refractory metal by electron bombardment. Good vacuum conditions are secured by the presence on the collector of a liquid air trap and ionization gauge. A negative potential of 45 volts on the suppressor ring prevents slow electrons from leaving the collector. The collector and associated circuits are insulated to prevent leakage currents.

The General Effect

The space current between the chamber and the target is the sum of several components, the most important of which are listed as follows:

A. Current originating on the target.
  (1) Secondary electrons.
  (2) Photoelectrons.
B. Current originating on the chamber.
  (3) Photoelectrons.

A soft radiation produced at the target by the ion bombardment[3] is the cause of the photocurrents, and these two currents must be of almost equal magnitude since the target and the chamber subtend equal angles at the source of radiation. The ratio of the space current i, and the ion current I, is dependent upon the potential of the chamber with respect to the target. This dependence is shown in Fig. 2. If the potential is sufficiently positive the photoelectrons generated on the chamber will be almost completely suppressed and the space current will consist of components (1) and (2) which are indistinguishable experimentally. It has a saturation value for chamber potentials more positive than V_s. For potentials more negative than V_p the current is made up of photoelectrons from process (3) with the other components practically

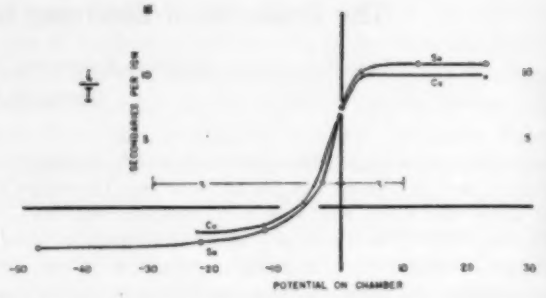

Fig. 2. Ratio of space current to ion current as a function of chamber potential, with 1.32 mv ions.

suppressed. The magnitude of these ratios is noteworthy.

These slow electron currents are the source of other currents of slow electrons of about 30 percent of the primary intensity,[4] but these secondary currents are suppressed by the saturation potentials and therefore do not affect the saturation values of i/I. These electrons with the more plentiful components (1), (2) and (3) will all be present when the chamber potential is between V_s and V_p and this complexity makes an accurate measure of the distribution in energy of any component quite impossible. It appears that the average energy of the electrons from the target is about 3 volts and about 10 percent have energy definitely greater than 10 volts. About 30 percent of these target electrons are photoelectrons.

Efficiency of Secondary Production

The average number of secondaries per ion is roughly reproducible from one sample to another of a given metal. The commonly used metals such as nickel, copper, molybdenum, aluminum, tungsten, silver, tin, magnesium and cadmium do not differ greatly one from another in efficiency if they have been well cleaned mechanically and observed under good vacuum conditions. Thus the emission from targets of these metals is likely to fall in the range of about 7 to 20 electrons per ion when they are bombarded by mercury ions in the energy range 0.7 to 2.35 mv.

[3] W. M. Coates, Phys. Rev. **46**, 542 (1934).

[4] H. E. Farnsworth, Phys. Rev. **31**, 405 (1928).

Dependence upon Experimental Conditions

The dependence of emission upon the energy of the mercury ions is shown in Fig. 3, which is a plot of the average number of secondaries per ion against the energy of the bombarding ions.

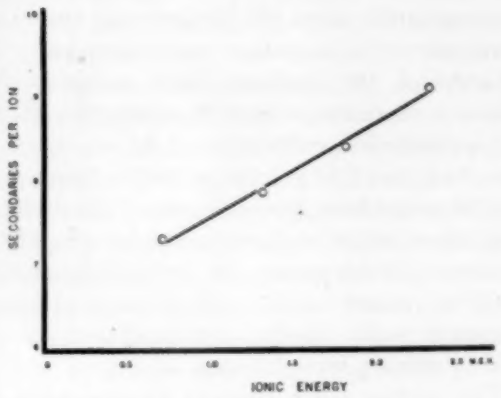

Fig. 3. Dependence of emission upon ionic energy.

Other data taken over the same energy range have shown the slope of increasing emission to be as much as three electrons per ion per million electron volts, so the only definite conclusion to be drawn from the rather meager data is that the emission does definitely increase with ionic energy.

Surface conditions

Although the surface conditions of a target cannot be very well known, there are certain treatments a target can be given to alter its emission properties and allow fairly reproducible results. These experiments have included the outgassing of targets, and the evaporation of fresh films. By means of electron bombardment a target of molybdenum or tungsten could be heated to an orange glow for many minutes until the evolution of gas had become very weak. Observations were begun about four minutes after heating was stopped, and the emission was from 50 to 75 percent of the values found for targets which had not been heated, but cleaned only mechanically or chemically. It rose steadily and after 20 or 30 minutes had reached a constant value only slightly lower than the emission from targets not heated.

Freshly formed alkali metal films

These targets were formed by distilling the alkali through a number of constrictions and thence onto the target, which could be seen during the formation of the film; the films appear to be thick, shiny, and sometimes a bit granular. The pressure was about 5×10^{-5} mm of Hg during evaporation, and fell to about 5×10^{-6} in three or four minutes after evaporation ceased. Fig. 4 shows the average emission per ion as a function of time after the film was formed. The nickel curve was taken simultaneously with the sodium curve, and is a standard of comparison.

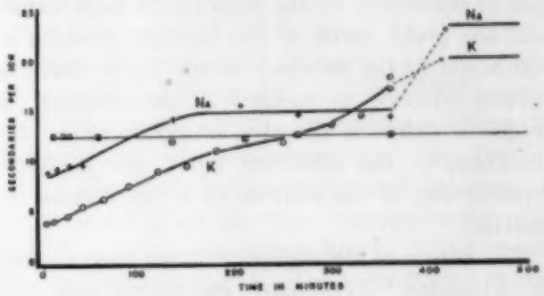

Fig. 4. Effect of elapsed time on freshly formed targets of alkali metals, with 1.32 mv ions.

The lithium targets were formed by evaporation from a pellet which was heated by a conical tungsten filament. The pellet with its oxide coating was outgassed for a considerable time at a fairly low temperature, then the temperature was gradually raised until the oxide coating cracked and rapid evaporation began. The pressure of about 10^{-4} mm of Hg during evaporation fell rapidly to 5×10^{-6} as in the case of the other alkalis. The appearance of the lithium films was thick and shiny, but somewhat darker than the others. The experimental values for the emission from lithium were somewhat higher than those given in Fig. 5, and have been reduced using nickel as a standard.

Discussion of Results

The rapid increase of emission with elapsed time and the differential effect with the pressure as shown in Fig. 5 indicate a relation between emission and gas pressure which is evidence for an adsorption theory as the explana-

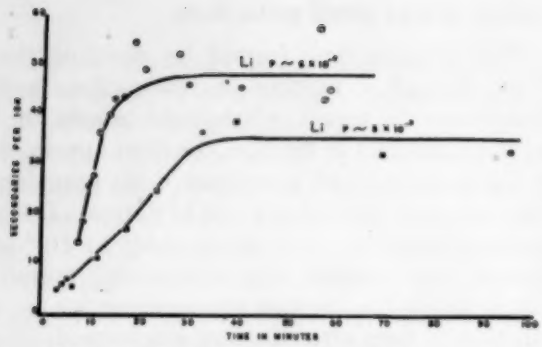

FIG. 5. Effect of elapsed time on freshly formed lithium targets, with 1.32 mv ions.

tion of the effect. In the light of the high values and the great speed of the lithium reaction as compared to the others it seems likely that the surface change is neither a modification of properties that is directly proportional to the thickness of the adsorbed layer, nor a simple replacement of the lithium by a gas film as the emitter.

The action of the alpha-rays has been studied by Thomson,[5] Logeman,[6] Bumstead and McGougan,[7, 8] Becker[9] and others, and it has been found that the number of secondaries per alpha-particle is of the order of 10, but depends upon experimental conditions. The energies of the secondaries lie in the range zero to two or three thousand electron volts with the great majority having a value of only a few volts; these energies are compatible with the theory that the maximum velocity a secondary can have is twice the velocity of the incident alpha-particle. This allows a maximum energy of about 10 volts for the secondaries produced by 1.32 mv. mercury ions, but about 10 percent of the electrons leaving the target have greater energy. It seems likely that these more energetic particles are photo-electrons. In this connection it should be pointed out that Coates[3] has found that x-rays of several thousand volts energy are produced by the swiftly moving mercury ions.

The author takes pleasure in expressing his gratitude to Professor Ernest O. Lawrence who suggested the problem and has been an inspiration and the source of invaluable suggestions.

[5] J. J. Thomson, Proc. Camb. Phil. Soc. **8**, 49 (1904).
[6] W. H. Logeman, Proc. Roy. Soc. **A78**, 212 (1906).
[7] H. A. Bumstead, Phil. Mag. **26**, 233 (1913).
[8] H. A. Bumstead and A. G. McGougan, Phil. Mag. **24**, 462 (1912).
[9] A. Becker, Ann. d. Physik **75**, 217 (1924).

FEBRUARY 15, 1935 PHYSICAL REVIEW VOLUME 47

The Effect of Pressure on the Electrical Conductivities of the Alkalies

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The observed effects of pressure on the resistance of lithium and of sodium are explained by taking into account the change of binding of the conduction electrons of these metals with pressure. A method of interpreting the experimental results is given and it is shown that from the theoretical calculations of Slater and of Millman one can predict the observed behavior of these metals. Thus no special assumptions are necessary to explain the "abnormal" behavior of lithium.

INTRODUCTION

IT is well known that the alkalies in common with most other metals become better conductors of electricity when compressed, with the notable exception of lithium, which becomes a poorer conductor under pressure than at zero pressure. Besides lithium, calcium and strontium also display an abnormal pressure coefficient of resistance, but these elements are divalent and this abnormal behavior can readily be explained.[1] The normal effect has been qualitatively explained by Grüneisen[2] as follows: When a metal

[1] See N. F. Mott, Proc. Phys. Soc. **46**, 691 (1934).
[2] Grüneisen, Verh. d. D. physik. Ges. **15**, 186 (1913).

is subjected to high pressure, the atoms are held in equilibrium positions which are closer together than at zero pressure, and the forces which hold the atoms in these positions are stronger than at normal separation. Hence, for a given thermal energy, the amplitudes of oscillations of the atoms decrease with increasing pressure, and since the scattering of the conduction electrons by the lattice varies with these amplitudes, we should expect a decrease in resistance when the metal is compressed.

The wave-mechanical theory of the structure of sodium and lithium,[3] and the modern theory of electrical conductivity[4] have been developed sufficiently so that we are in a position to attempt an explanation of the pressure effects in these metals. According to a general theorem of Bloch, the state of an electron in a metallic lattice is defined by a wave function of the form

$$u = e^{i(\mathbf{k}\cdot\mathbf{r})}\psi_{\mathbf{k}}(x, y, z)$$

with an energy E which is a function of the components of the vector $\mathbf{k}$. For free electrons, $\mathbf{k}$ is the wave vector and is proportional to the momentum of the electron. In the case that the energy E is a function only of the magnitude of $\mathbf{k}$, a condition which is well fulfilled for Na and Li for the values of $\mathbf{k}$ which determine the conductivity, Bethe gives the following expression for the conductivity σ at high temperatures,

$$\sigma = \frac{n_0}{\pi^3}\frac{k}{C^2}\left(\frac{dE}{dk}\right)^2\frac{2\pi k_0}{ha_0}\frac{M}{m}\frac{\Theta^2}{T}. \qquad (1)$$

In this expression n_0 is the number of conduction electrons per atom, k_0 Boltzmann's constant, a_0 the radius of a hydrogen atom, M the mass of the metallic ion, Θ the Debye characteristic temperature. The quantities k, dE/dk refer to the maximum of the Fermi distribution and C is a constant which measures the scattering power of a metal ion.

For the purpose of discussing the variation of conductivity with pressure, we may write Eq. (1) more conveniently as

$$\sigma \sim (k/C^2)(dE/dk)^2\Theta^2, \qquad (1a)$$

all the other factors being independent of pressure for a given metal. The characteristic temperature Θ increases with increasing pressure (the Grüneisen effect mentioned above), and we must attribute the abnormal behavior of lithium to changes in the other factors.

1. Interpretation of the Experimental Results

The changes of resistance of most of the metals under pressures up to 12,000 atmospheres have been measured by Bridgman.[5] In the case of sodium, he finds that the electrical resistance drops (at 12,000 atmos.) by about 57 percent from its value at zero pressure, whereas for lithium, the electrical resistance increases by about 9 percent under the same conditions. In order to compare the experimental results with the theory, it is necessary first of all to correct for the factor Θ^2 in (1a). The variation of Θ with pressure may be obtained with the help of the thermodynamic relation[6]

$$(1/\Theta)(\partial\Theta/\partial p)_T = (1/C_v)(\partial V/\partial T)_p,$$

where V is the volume of the metal and C_v its heat capacity at constant volume. This relation may also be written as

$$(\partial \ln \Theta/\partial p)_T = \beta/c_v,$$

with β the thermal expansion coefficient of the metal, and c_v the heat capacity per unit volume. c_v may be considered constant up to pressures of 20,000 atmos., but β decreases rather sharply with pressure. The variation of β with pressure has been determined by Bridgman.[7] For lithium, β decreases by about 50 percent at a pressure of 20,000 atmos., and for sodium, by about 60 percent. With the help of these results, one may directly calculate the variation of Θ with pressure and hence values of σ/Θ^2 as a function of pressure.

[3] J. C. Slater, Rev. Mod. Phys. **6**, 210 (1934); Phys. Rev. **45**, 794 (1934); Also see the following paper by J. Millman.

[4] See the article by A. Sommerfeld and H. Bethe, Handb. d. Physik **XXIV**/2 (1933).

[5] P. W. Bridgman, Proc. Am. Acad. Arts and Sci. **56**, 61 (1921).

[6] Grüneisen, Handb. d. Physik **10**, Chapter 1 (1926).

[7] I should like to express my thanks to Professor Bridgman for supplying me with these as yet unpublished experimental values.

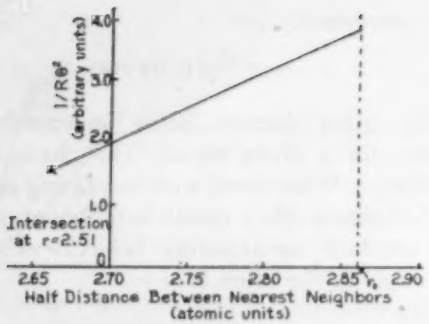

FIG. 1. $1/R\Theta^2$ plotted as a function of half distance between nearest neighbors for lithium.

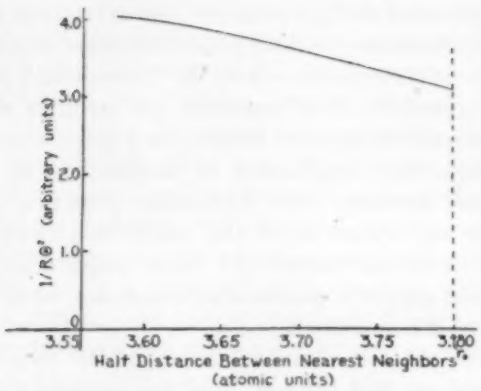

FIG. 2. $1/R\Theta^2$ plotted against half distance between nearest neighbors for sodium.

For reasons which we shall discuss in the next section, it is more convenient for our purposes to calculate $1/R\Theta^2$ as a function of pressure, where R is the measured resistance of the metal sample, uncorrected for the changes in volume due to pressure. The results are shown in Figs. 1 and 2 for Li and Na, respectively, where $1/R\Theta^2$ in arbitrary units is plotted as a function of the lattice constant, or more precisely, as a function of r, the half distance between nearest neighbors in the lattice. The conversion of the independent variable from pressure to r is easily made with the help of the known compressibilities of these metals. For Li the decrease of $1/R\Theta^2$ with r is practically linear up to 20,000 atmos., whereas for Na, there is a rise in $1/R\Theta^2$, and there seems to be an indication that the curve is approaching a maximum.

2. Comparison of the Experimental Results with the Theory

To obtain a comparison of experiment and theory, we refer again to the relation (1a) which we rewrite as

$$\sigma/\Theta^2 \sim (k/C^2)(dE/dk)^2.$$

If the metal sample has a length l and cross section A, the resistance R is related to the conductivity σ by $R=(1/\sigma)(l/A)$, or $\sigma=(1/R)\cdot(l/A)$, so that we may write

$$(1/R\Theta^2)\cdot(l/A) \sim (k/C^2)(dE/dk)^2.$$

Now the number of conduction electrons per unit volume (equal to the number of atoms per unit volume for the alkalies) varies as the cube of k, so that k itself varies inversely as the linear dimension of the crystal. Thus, the variations of l/A and k with pressure cancel, and we have as a final result

$$1/R\Theta^2 \sim (1/C^2)(dE/dk)^2.$$

As far as order of magnitude is concerned, it seems reasonable to place C independent of pressure over the range utilized in the experiments, and to compare directly the values of $1/R\Theta^2$ as shown in Figs. 1 and 2, with the theoretical values of $(dE/dk)^2$.

In the case both of Na and Li, the first Brillouin zone is half full and up to this point the energy can be taken practically independent of the direction of the wave normal. If one plots E *vs.* k for the first zone, one obtains the familiar curve shown in Fig. 3. The curvature of the parabolic portion which alone interests us is almost that for free electrons in the case of sodium, but much less in the case of lithium, indicating a tighter binding of the electrons in the latter metal. Now the slope dE/dk at the edge of the Fermi distribution will clearly decrease as the energy breadth of the first Brillouin zone decreases. In Figs. 4 and 5 are plotted the lowest energy states for Li and Na, respectively, as function of the half distance between nearest neighbors in the lattice. On these curves the breadth of the first Brillouin zone ΔE is indicated at normal separation. If we now imagine the metals compressed, we see that for Li the breadth ΔE of the zone decreases and hence dE/dk decreases. This behavior was first pointed out by Professor Slater as a means of

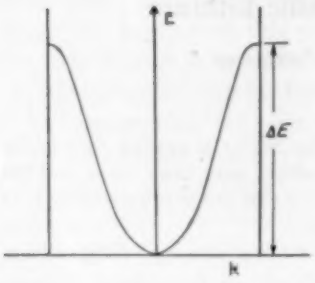

FIG. 3. Energy *vs.* wave number in the first Brillouin zone.

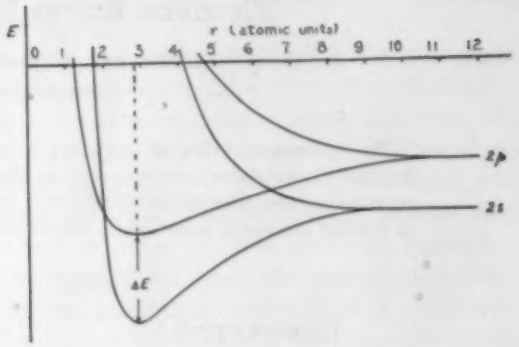

FIG. 4. Energy bands for Li *vs.* half distance between nearest neighbors.

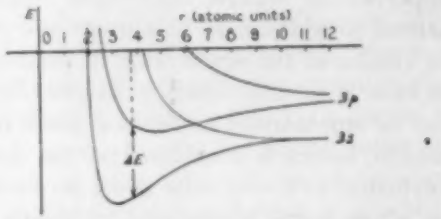

FIG. 5. Energy bands for Na *vs.* half distance between nearest neighbors.

explaining the abnormal pressure coefficient of lithium. At about 2.1 atomic units, where the lowest $2s$-state and the lowest $2p$-state intersect, we should expect the slope to become zero. On the other hand, in the case of sodium, the breadth of the zone increases somewhat with decreasing r and then eventually gets smaller. Thus, we should expect an initial increase in the freedom of the electrons for sodium as it is compressed and eventually a decrease as it is compressed further. Although it has not been possible to attain pressures high enough to cause a reversal in the resistance-pressure curve for sodium,[8] such a behavior has been observed by Bridgman[5] for Cs, and this affords a very satisfactory check on the general theory.

Turning now to the quantitative aspects, Mr. Millman has kindly calculated the slopes dE/dk as a function of r for propagation in the 110 direction for Li. This indicates a drop of about 10 percent at a pressure of 12,000 atmospheres, and hence $(dE/dk)^2$ drops by about 20 percent at this pressure. From Fig. 1 we see that at $r=2.78$ atomic units (corresponding to $p=12{,}000$ atmos.) there is a drop in $1/R\Theta^2$ of about 25 percent. Thus, we find a satisfactory check for this phenomenon. If one extrapolates the curve in Fig. 1, it indicates infinite resistance for about $r=2.5$ units, whereas Millman's calculations give 2.1 units. The reason for this discrepancy is easy to give. The calculations for lithium were made using a potential function for the free atom. This is only a rough approximation, and gets worse as the metal is compressed. Certainly the real potential curve lies lower in the metal than in the free atom, and we should accordingly expect the lowest $2p$ level to drop faster and intersect the lowest $2s$ level at larger separation than 2.1 units. In sodium, the free atom potential is a much better approximation at the actual distance of separation, since the lattice constant of sodium is much larger than that of lithium. The observed increase in $1/R\Theta^2$ with increasing pressure corresponds to the predicted initial increase of ΔE. Furthermore, the fact that the rate of increase of $1/R\Theta^2$ decreases as the pressure increases, indicates that at higher pressures ΔE will decrease as expected.

To summarize, we may say that wave mechanics has led to a satisfactory explanation of the observed pressure effect on resistance for the alkalies, including the abnormal behavior of lithium, without any special assumptions, and predicts the correct order of magnitude of these changes. When one takes into account the approximate nature of the theory, the fact that it holds at the absolute zero and that the experimental results are obtained at room temperature, the quantitative agreement between theory and experiment must be regarded as highly satisfactory.

[8] Professor Bridgman has informed me that such a reversal would take place at about 24,000 atmospheres.

Electronic Energy Bands in Metallic Lithium

J. MILLMAN, *Massachusetts Institute of Technology*

(Received December 19, 1934)

The extension of Wigner and Seitz's method developed by Slater is applied to metallic lithium. Calculations corresponding to those of Slater for sodium have been made and the results discussed. One essential difference between these metals is that the conduction electrons in lithium are much more tightly bound than those of sodium.

INTRODUCTION

WIGNER, Seitz and Slater[1] have developed a method for calculating the electronic properties of metals and have applied this method to sodium. In this paper are presented the results of the application of their theory to the case of metallic lithium. Briefly, the method may be summarized as follows: Each ion in the metallic lattice is considered at the center of a polyhedral cell, the cells being so formed that the whole metal is obtained by tightly packing them together. In the case of a body centered lattice, which is the structure of all the alkali metals, these cells are truncated octahedrons formed by the intersections of planes which perpendicularly bisect lines joining an ion with its eight nearest and its six next nearest neighbors. Within each of these cells the potential is assumed to have spherical symmetry. In a simple translation from a point on one face of the polyhedron to the perpendicularly opposite point on the opposite face the wave function of an electron, according to a general theorem of Bloch,[2] will have become multiplied by $e^{2\pi i\mathbf{p}\cdot\mathbf{n}/h}$, where $\mathbf{p}$ is the momentum which the electron would have if it were free and where $\mathbf{n}$ is this lattice translation. The problem thus reduces to one of spherical symmetry within each cell together with the boundary conditions that the wave function and its gradient at a point on one face be equal to their value at the corresponding point of the opposite face multiplied by $e^{2\pi i\mathbf{p}\cdot\mathbf{n}/h}$. Then the wave function at any point of another cell is obtained by considering a point within the primary cell such that the distance between these two points is an integral number of lattice translations and then applying the Bloch theorem.

In order to satisfy the boundary conditions at every point on the surfaces of the polyhedrons it would be necessary to choose a wave function which is a linear combination of all the solutions of the spherically symmetric Schrödinger equation. As a first approximation we fit the boundary conditions only at the midpoints of the faces between an ion and its eight nearest neighbors. We then use a linear combination of eight s, p, d and f functions which do not vanish at all the midpoints in question and are led to a set of linear homogeneous algebraic equations from which the constants are to be determined. In order that these have a nonvanishing solution the secular determinant must equal zero and this yields the relation between p_x, p_y, p_z and the one electron energies E.

I. ENERGY BANDS FOR LITHIUM

The potential field employed for lithium was that for the free atom.[3] The use of such a potential at the actual internuclear distance is justifiable only as an approximation. In the immediate neighborhood of the nuclei the real potential and that for the free atom should be very nearly identical, but at larger distances there will be considerable difference. In fact the normal derivative of the potential must vanish at the boundary surface between two cells, since on the average the net charge within each cell is zero and hence the force on an electron at this boundary must vanish. The true potential

[1] Wigner and Seitz, Phys. Rev. **43**, 804 (1933); J. C. Slater, Phys. Rev. **45**, 794 (1934); Rev. Mod. Phys. **6**, 210 (1934).

[2] For a direct proof of this theorem see Sommerfeld and Bethe, Handb. d. Physik **XXIV**/2, p. 370.

[3] I wish to express my thanks to Dr. F. Seitz who kindly supplied me with this potential.

thus lies lower than that for the free atom and the error made by neglecting this difference increases with decreasing internuclear distances. A better approximation would be to employ essentially the potential for the free atom rounded off and depressed so as to join smoothly with the potential of a neighboring cell.

The Schrödinger equation was integrated numerically for a series of energy values. In this way the radial functions s, p, d and f (for $l=0$, 1, 2 and 3, respectively) were obtained, and from these Fig. 1 was constructed. The energy is plotted as a function of half distance between nearest neighbors, the curves shown being those for which $s=0$, $s'=0$, $p=0$, $p'=0$, etc., where s, p, d and f denote the values of the radial functions at the surface of the cell and s', $p'\cdots$ the corresponding derivatives. The half distance between nearest ions is experimentally found to be 2.86 atomic units (indicated on the diagram by the dotted vertical line) and it is seen that the minima of the lowest $s'=0$ and $p'=0$ curves occur at just about this point. One very significant difference between these curves and the corresponding ones for sodium is that the minimum of the $p'=0$ curves is much lower than for sodium. This causes this curve to cross the lowest curve at about 2.0 atomic units whereas for sodium this crossing does not occur until we get to much smaller internuclear distances. It is just this difference which explains the abnormal pressure coefficient of resistance of lithium.[4]

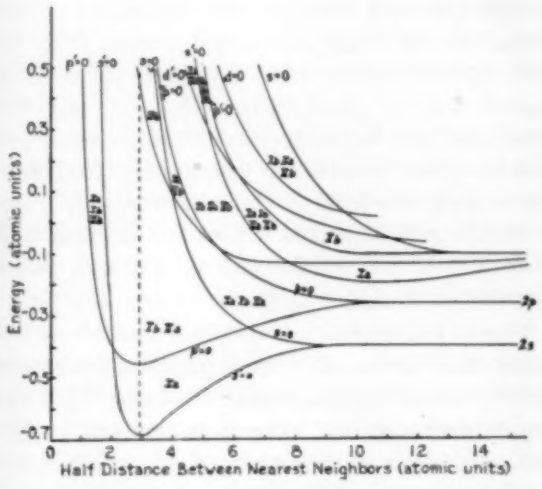

FIG. 1. Energy plotted against half distance between nearest neighbors for lithium.

By restricting ourselves to the x-y plane of momentum space ($p_z=0$) we can explicitly obtain the allowed types of wave functions. Slater showed that for this case the eight linear equations break up into two sets of four each so that solutions are possible by placing the determinant of one set equal to zero and also equating the constants of the other set equal to zero. We call the two possibilities Case I and II, respectively. For Case I we have real propagations for some directions provided that either $ps'/p's$ or $pd'/p'd$ is negative. These two cases are labeled Ia and Ib, respectively. Similarly real propagation of type IIa and IIb is possible providing that $pd'/p'd$ or $fd'/f'd$ is negative. The regions in which the different types of propagation enumerated above can occur are indicated in Fig. 1. Of course, one can find such regions by seeing what sign s, s', p, $p'\cdots$ have for each energy and internuclear distance, but it is simpler to proceed as follows: For very large distances the energy bands degenerate into the energy levels of the free atom and therefore in the neighborhood of these levels are regions in which propagation is not possible in any direction. In other words, here $ps'/p's$, $pd'/p'd$ and $fd'/f'd$ are all positive. Such a region is seen in Fig. 1 surrounding the $2s$ level. Now, as we cross the line $s'=0$, $ps'/p's$ must change sign and is now negative, allowing type Ia. As we pass from this region across the $p'=0$ curve $ps'/p's$ and $pd'/p'd$ must change sign, so that $ps'/p's$ now becomes positive again whereas $pd'/p'd$ is now negative and only types Ib and IIa are allowed. By similar reasoning we can assign the other regions of Fig. 1 to the various cases as indicated. The regions which are not marked are those for which we have no real propagation in any direction. However, even for the other regions there are certain directions for which we have no propagation. For a detailed discussion of how these gaps come about we refer to Slater's paper. The following example will serve as an illustration. Consider the normal distance of separation and a momentum vector ending at the edge of the first zone in the 110 direction. Then an inspection of Slater's equations tells us that the corresponding energies

[4] See the preceding paper.

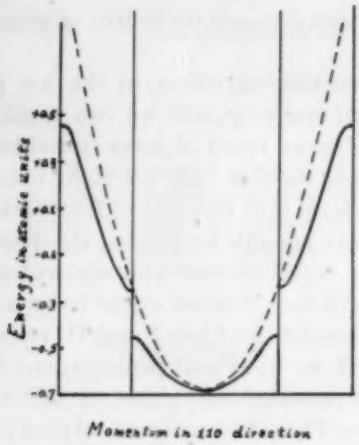

FIG. 2. Energy plotted as a function of momentum in the 110 direction.

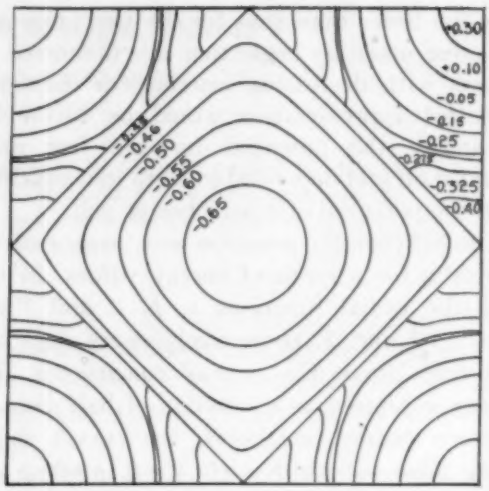

FIG. 3. Constant energy contours in x-y plane of momentum space.

occur at either $p'=0$ or at $sd'+ds'=0$. Since we have two energies corresponding to the same momentum at the edge of the zone this must mean that we have a gap in energy here. This is clearly seen in Fig. 2 where the energy is plotted as a function of the magnitude of momentum in the 110 direction. The first two zones are indicated and the gap comes at the vertical lines which represent the boundary between these zones. For lithium one finds that the $p'=0$ condition comes for a lower energy than the $sd'+ds'=0$ condition and hence $p'=0$ corresponds to the top of the first band whereas $sd'+ds'=0$ is the bottom of the second band. For sodium just the reverse is true.

If we plot curves of constant energy in the p_x-p_y plane we obtain Fig. 3 for the first two Brillouin zones at the normal distance of separation. The center of the first zone comes at about $E=-0.68$ atomic units and the corner of the second at about $E=+0.46$ atomic units, a much wider range than is covered in sodium. The first zone goes to the $2s$ level of the free atom at infinite separation and the second goes to the $2p$ level. There is a marked difference in appearance between this figure and the corresponding one for sodium. Near the center of the diagram the curves are approximately circular, but they flatten out and become parallel to the edge of the first zone as we approach this edge. For sodium they stay more nearly circular (free-electron-like) all the way out except very close to the edge of the zone where there is the gap in energy spoken about above. The difference in the shapes of the constant energy curves for lithium and sodium is due mainly to the fact that the gap comes in the second zone for lithium whereas it occurs in the first zone for sodium.

Let us now examine Fig. 2 in more detail. The dashed curve is the free electron parabola ($E=p^2/2m$) and it is seen that the solid curves are much flatter than this, indicating that the conduction electrons in metallic lithium are none too "free." As a matter of fact, at the edge of the Fermi distribution the ratio of the slopes of the two curves (which measures the freedom of the electrons) is about $\frac{1}{2}$, whereas for sodium its ratio is very nearly 1. An inspection of the shape of the constant energy curves (Fig. 3) tells us that in any other direction the E *vs.* p curves will be even flatter than in the 110 directions and hence the electrons are even less free for these directions. Furthermore, whereas for sodium the energy gap extends only from -0.37 to -0.32 atomic units, for lithium it is from -0.45 to -0.26 atomic units, a jump almost four times as large.

Due to the periodicity of energy in momentum space the curves of Fig. 2 can be continued periodically along the axis of abscissas. Then the upper curve would have a maximum at the center of the first zone while the lower curve has a minimum there. This is what is usually found, the minima occurring for bands which go to

s-states at infinite separation and the maxima for bands which go to p-states.

II. The Wave Functions

In Fig. 4 are plotted a number of typical wave functions in the first band. The dots represent nuclei along the 111 direction, this being the direction of closest packing. The wave normal is in the 110 direction ($p_x = p_y$, $p_z = 0$). The dashed curves are the wave functions of free electrons having the same p value as the actual curve. It is seen that, whereas near the nuclei the two do not agree at all, in the region between ions we have wave functions which are fairly free-electron like. This is our justification for using the metallic correspondence, that is, for assigning the $2s$ electrons rather than the bound $1s$ electrons to the first zone of momentum space. Physically, this is just what we should expect. The bound electrons are confined to regions of low potential around the nuclei and hence are traveling much faster than the free electrons. Therefore, their p-values must be larger than those of the $2s$ electrons.

A comparison with the wave functions for sodium again indicates that lithium is far less free-electron like than sodium. This means that the metallic correspondence is much better for sodium than for lithium. In other words, if we were to look at the momentum eigenfunctions for the $2s$ electrons of metallic lithium we would not find that they had simply a peak for one value of p in the first zone and were practically zero everywhere else, but rather that they had appreciable values for several cells of momentum space.

Let us examine the wave functions more closely. At the center of the first zone, ($p = 0$, $\lambda = \infty$), we have a standing wave (that is, a real instead of a complex wave function) which is simply an s function repeated periodically throughout the lattice (Fig. 4a). It is interesting to note that for a large part of the volume the wave function is constant. (A free electron wave function with $\lambda = \infty$ would be constant everywhere.) As we decrease the wavelength we obtain successively the traveling waves Fig. 4b, c, d and e. Then at the edge of the first zone, where the wavelength is just twice the distance between nearest neighbors we obtain a standing wave, Fig. 4b. This means zero current, corresponding physically to Bragg reflection of the electron wave. One sees that whereas the lowest level of the first band is an atomic s-state (repeated periodically) and the highest an atomic p-state (repeated periodically) the intermediate levels are linear combinations of s, p and d functions. If one examines the nodes of the functions one observes that some come from the atomic states and some are due to the modulating sine and cosine functions.

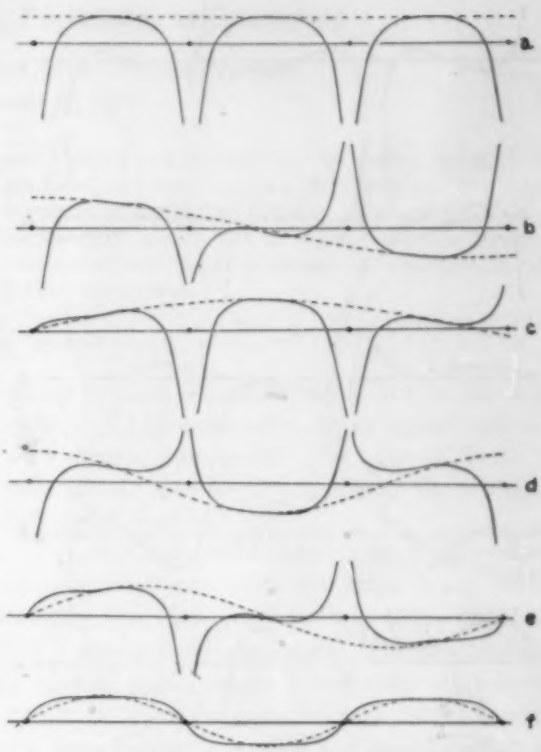

Fig. 4. Wave functions for free electrons for lithium as a function of distance along 111 direction, first band, type Ia.
a. $2s$ function $E = -0.68$, $p = 0$, $\lambda = \infty$. Real function.
b.c. Real and imaginary parts. $E = -0.65$, $\lambda = 31.8$ atomic units.
d.e. Real and imaginary parts. $E = -0.55$, $\lambda = 17.1$ atomic units.
f. $2p$ function. End of first zone $E = -0.45$. Wavelength is twice distance between nearest neighbors.
The dashed curves indicate sinusoidal wave functions having the same wavelength as the actual function.

Fig. 5 shows wave functions of type Ib in the second band, and it is seen that we again have standing waves at the beginning and end of the zone. 5a is formally related to 4f as the real and imaginary parts of a wave function, 5a resembling a sine curve and 4f a cosine curve. As mentioned above, for sodium the reverse is

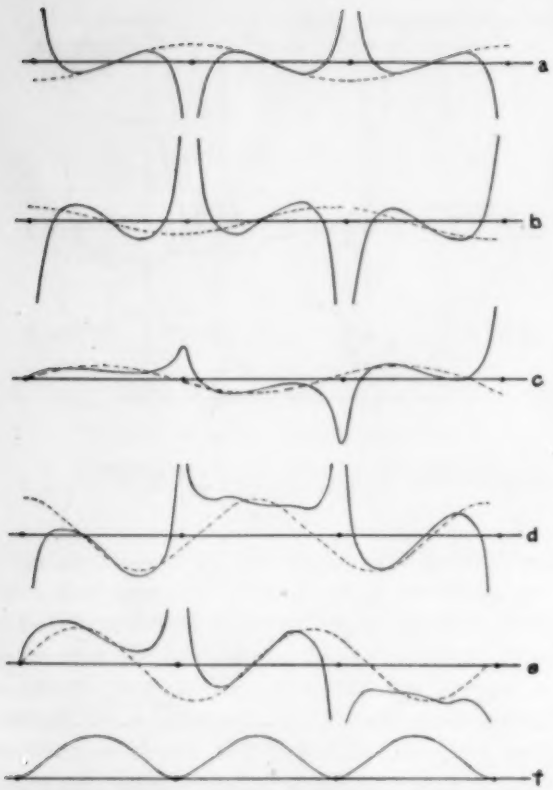

FIG. 5. Wave functions for free electrons for lithium as a function of distance along the 111 direction, second band, type Ib.
a. Beginning of second band. $E=-0.26$, λ is twice distance between nearest neighbors.
b.c. Real and imaginary parts, $E=-0.25$, $\lambda=10.8$.
d.e. Real and imaginary parts, $E=-0.05$, $\lambda=8.40$.
f. Standing wave at end of second zone. $E=+0.46$, λ is just the distance between nearest neighbors.

true, namely, the sine-like wave function (satisfying the condition $sd'+d's=0$) comes at the end of the first zone and the cosine-like function (satisfying the condition $p'=0$) at the beginning of the second. Now as we move away from the edge of the zone to higher energies we obtain the remaining curves of Fig. 5 and it is seen that the agreement with the free electron wave functions gets poorer and poorer. At the end of the zone, where the wave is simply a d-function the agreement is so bad that no free electron curve is even indicated on 5f. At first this may seem strange since we should expect that as the energy of an electron was increased it would become more and more free. However, we must remember that we have assigned that part of momentum space about the origin to the $2s$ electrons and we have said that the $1s$ electrons are traveling faster than these and hence have momentum values further out from the origin. It is only for energies higher than those of the bound electrons that we can expect wave functions which closely resemble sinusoidal waves, that is, momentum eigenfunctions which have an appreciable value for only one cell lying relatively far from the origin.

We must therefore conclude from the wave functions as well as from the shapes of the constant energy curves in momentum space and the E *vs.* p diagram that the conduction electrons in lithium are much less free than those in sodium.

A few remarks about the approximations made should be added. The assumption of spherical symmetry around each ion has been discussed by Wigner, Seitz and Slater.[1] They show it to be a consistent one which should be very nearly the truth for the type of lattice involved. The worst approximation made, however, is the fitting of the boundary conditions at only eight points instead of all over the polyhedral surface with which we have surrounded each ion. It would be very interesting to fit the boundary conditions midway between second nearest neighbors also; that is, at the center of every face of the polyhedrons. Such a refinement will undoubtedly modify the shape of the energy contours of Fig. 3 near the edge of the zone. For example, we should no longer expect to find the boundary a surface of constant energy.

I should like to express my thanks to Professor J. C. Slater for suggesting this problem.

The Hall Effect in Sodium, Potassium and Caesium

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The Hall effect has been studied in carefully purified samples of sodium, potassium and caesium obtained by distilling the metals in vacuum, into thin flat molds of Pyrex, with sealed-in electrical leads. The Hall constants determined are as follows: sodium, −0.0021, potassium −0.0042, caesium, −0.0078. The Hall effect in each case was found to be independent of the current density in the specimen, and of the magnetic field intensity. The change in resistance due to the magnetic field was too small to be observed, up to a field of 20,000 gauss. The theory of Sommerfeld and Frank is considered in connection with lithium and sodium.

THE Hall constant for lithium[1] and sodium[2] has been determined, but there is no record of measurement of the effect in the other alkali metals. This fact is no doubt due to the difficulties that arise in obtaining in pure form the thin strips of the metal required for this measurement, and at the same time keeping them protected from the rapid action of the oxygen and water-vapor of the atmosphere. Since there is some interest in knowing the variation of the Hall effect in the alkali metals, and since only the effect for those of lowest atomic number has been found, it seemed worth while to attempt to devise a method for working with the more chemically-active ones of higher atomic number, namely, potassium, rubidium and caesium.

The present experiments were begun with the idea of obtaining a sample of the metal in a flat, air-tight mold of glass, with all the electrical contacts sealed in. The scheme was to construct a mold, the cavity of which would be a pattern for the metal strip upon which the measurements were to be made. This mold could then be attached to a vacuum system and the desired metal distilled into it from a connected reservoir. Thus the metal obtained would have a minimum of contaminating material with it, would be free from absorbed gases and would be sealed away from the atmosphere in a convenient form for studying the Hall effect.

The devising of a satisfactory mold proved to be a much more difficult matter than was anticipated. Several different methods were tried. It seemed at first that it should be relatively simple to cement together properly-spaced glass plates to form a suitable mold, but of the wide variety of adhesives used, none proved suitable, since it was impossible with any of them to maintain a vacuum-tight seal over the temperature range required.

The type of mold finally used was made entirely of Pyrex, with tungsten leads sealed directly into the glass for electrical contacts. Fig. 1 shows the arrangement. The construction of one of these molds was briefly as follows. Plates of Pyrex, approximately $10\times3.2\times0.35$ cm, were carefully ground flat, and bevelled on the edges. These plates were held together with a special clamp, the four accurately ground Pyrex spacers S keeping the desired distance between them. Then, while they were maintained at a temperature of 400° to 500°C by means of Bunsen burners which played on a metal cradle surrounding them, their edges were fused with an oxyhydrogen flame, and the end tubes attached. When the mold had cooled, holes were drilled at H for the side leads, after which it was heated again and the side tubes A, B, C, with their tungsten leads, sealed on. Finally the whole mold was carefully annealed in an oven, and it was ready to attach to the vacuum system for filling.

The object of attaching side-tubes instead of letting the tungsten extend into the strip proper, was to assure good contact between the metal and the tungsten (a large surface being in contact in this way) and to avoid thermal effects which might arise if the tungsten reached into the strip carrying the primary current. It was hoped also to work with the liquid metal, where this arrangement should minimize the effects of convection currents.

[1] A. W. Smith, Phys. Rev. **8**, 79 (1916).
[2] A. v. Ettingshausen and W. Nernst, Ann. d. Physik [3] **29**, 343 (1886).

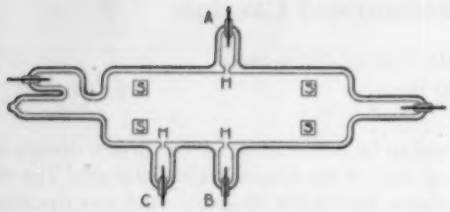

FIG. 1. Diagram of mold.

The thickness of the mold was determined by measuring the thickness of the plates at various places with a micrometer before fusing them together, and then measuring the over-all thickness of the mold at these designated points after fusing. In several cases the thickness was checked by breaking open the mold after using it and actually measuring the spacing with a micrometer microscope.

Measurements of the Hall e.m.f. (leads *A*, *B*, Fig. 1) and the longitudinal potential drop (leads *B*, *C*, Fig. 1), were made by means of a low resistance Wolff potentiometer *P*, using a galvanometer of sensitivity 30 mm per microvolt. A thin exploring coil, held permanently between the poles of the magnet, was used to determine the magnetic field intensity.

PREPARATION OF THE SAMPLES

The sodium and potassium were obtained by straining the molten metal through a nichrome mesh in vacuum, and then distilling it. This singly distilled metal was then transferred to the main vacuum system to which the mold was attached, and here it was twice distilled, the last distillation taking it into the mold. During distillation the mold was kept at a temperature of 350°C until the metal began to run in, when it was lowered to 150°C. Both metals distilled freely between 350°C and 400°C. During the last distillation the vacuum was at all times below 10^{-5} mm of mercury, showing that the gases had been thoroughly removed from the metal. The liquid metal flowed freely into the smallest recesses of the mold.

The caesium used was procured from the Research Laboratory of the General Electric Company. It was obtained by reducing CsCl with calcium. The caesium produced in this way obviously contained some calcium since the melting point proved to be below 15°C so that it was necessary to distill it for purification. Since caesium ignites immediately on being exposed to the atmosphere, it was put in a glass tube so constructed that it could be brought to our vacuum system and attached without unsealing the metal. After a vacuum was established, in order to let the caesium escape into the system, a thin glass bulb was broken by means of a piece of iron which had been placed in the tube and an electromagnet outside. The metal was twice distilled at a temperature of 250°C in a vacuum less than 10^{-5} mm, the McLeod gauge 'sticking' at all times during the process. At this temperature the caesium had very little effect on the glass (nonex), though the tube did become slightly brown in the first distillation. Only a small amount of the metal was driven over in the last distillation, and there was no evidence of attack on the glass. The final sample of the metal was a pale yellow in color, and it melted at approximately 28°C.

RESULTS

Sodium

The measurements of Ettingshausen and Nernst[2] were made on a strip of sodium which was worked while exposed to the atmosphere, and consequently the metal must have contained a great deal of absorbed gas with other contamination. For this reason it was decided to fill one of our molds with sodium as carefully prepared as possible and to measure the Hall constant for such a sample.

The pertinent data taken for sodium are summarized in Table I. The Hall e.m.f. given for

TABLE I. *Summary of data for sodium.* Thickness of mold =0.088 cm; temperature 25°C, *R* for sodium = −0.0021 e.m.u.

Primary current (amp.)	Flux density	P.D. (*A*, *B*) (volts×10^{-7})	Hall e.m.f. (volts×10^{-7})	*R* (e.m.u.)
6	0	1	29	
6	20,400	−28	30	−0.0021
6	−20,400	31		
8	0	5	39	
8	20,400	−34	40	−0.0021
8	−20,400	45		

each current represents the average of five or more readings.

The limit of error in the thickness of the mold is estimated to be 3 percent and in the Hall e.m.f. 3 percent. Since these are the predominant sources of error in the determination, the Hall constant found for the specimen used is probably in error not more than 6 percent. The values obtained by Ettingshausen and Nernst[2] were from -0.0023 to -0.0025. As Hall effect measurements go, the agreement is as good as could be expected, especially in view of the different treatment of the specimens used.

It was found that the constant obtained was independent of the field (from 2000 to 20,000 gauss) and of the primary current (1 to 8 amperes). The change in resistance in the magnetic field was too small to observe with our set-up. Melting the sodium and allowing it to solidify again did not alter the observed value of the constant.

Potassium

Five molds were filled with potassium. The first two were of our earliest construction, and the thickness for these was least accurately known. In addition, the potassium with which these were filled was from an unknown source and distilled but once. The potassium used in the other three molds was of the best obtainable from the stock of Eimer and Amend, and the measurements on these were at every stage more carefully taken than on the first two. For this reason the constants determined for the first two specimens are not considered in the final value given, though results for them are included below. A summary of data for a typical run for potassium is given in Table II. The Hall e.m.f. given for each current represents the average of five or more readings.

TABLE II. *Summary of data for typical run for potassium.* Thickness of mold = 0.082 cm; temperature 25°C. (Letters R and D refer to direction of primary current.)

Primary current (amp.)	Flux density	P.D. (A, B) (volts$\times 10^{-7}$)	Hall e.m.f. (volts$\times 10^{-7}$)	R (e.m.u.)
1 R	0	22		
1 R	20,400	11	11	-0.0042
1 R	$-20,400$	31	10	
2 R	0	44		
2 R	20,400	23	21	-0.0042
2 R	$-20,400$	65	21	
4 R	0	95		
4 R	20,400	136	41	-0.0042
4 R	$-20,400$	53	43	
6 R	0	144		
6 R	20,400	207	63	-0.0042
6 R	$-20,400$	81	63	
6 D	0	-159		
6 D	20,400	-222	63	-0.0042
6 D	$-20,400$	-96	63	
8 D	0	-213		
8 D	20,400	-127	86	-0.0043
8 D	$-20,400$	-298	85	

TABLE III. *Hall constant for various samples of potassium.* R for potassium $= -0.0042$ e.m.u.

Mold No.	Thickness	Hall constant
1	0.061 cm	-0.0046 e.m.u.
2	0.161	-0.0052
3	0.085	-0.0042
4	0.082	-0.0042
5	0.085	-0.0043

The results for the several samples of potassium used are given in Table III. For reasons given above the first two are not considered in the average.

The value of R for any one of the molds 3, 4, 5 is estimated to have a limit of error of 5 percent so that the average value should be considerably better than this.

Hall coefficient as function of primary current and magnetic field. It was found for the limits of the experiment that the Hall coefficient was independent of the magnetic field intensity and of the current through the specimen. In Fig. 2, the Hall e.m.f. for potassium is plotted against the impressed magnetic field.

Hall coefficient as function of temperature. Measurements of the Hall effect made over a range of temperature from -15°C to $+60$°C were obtained by heating and cooling the entire "magnet room" which had been built with a refrigerating unit for previous low temperature work in this laboratory. No measurable variation in the Hall coefficient was found in this temperature range.

Attempts were made to follow the Hall e.m.f. from the solid to the liquid state, but each time the readings became quite unsteady as the melting point was reached (due likely to convection currents which gave rise to thermal

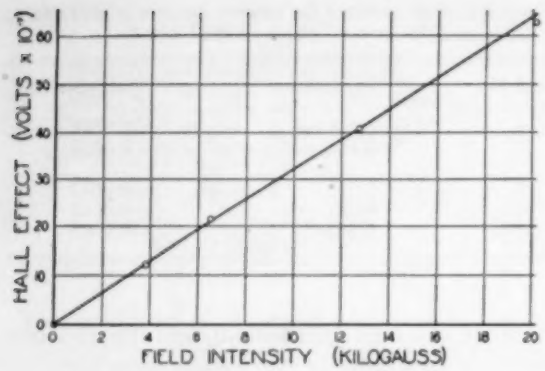

FIG. 2. Hall e.m.f. as function of field intensity (potassium).

e.m.f.'s) so that no consistent data were obtained.

Caesium

In making measurements on the caesium sample the temperature between the magnet poles was kept at approximately −5°C by means of dry ice so that the metal would not melt when the primary current was maintained. Due to this arrangement there were thermal effects in the leads, which made the measurement of the Hall e.m.f. less accurate than for the other metals, as is evident from the summary of data given in Table IV.

TABLE IV. *Summary of data for caesium.* Thickness of mold = 0.078 cm; temperature = −5°C. R for caesium = −0.0078 e.m.u.

Primary current (amp.)	Flux density	P.D. (A, B) (volts×10^{-7})	Hall e.m.f. (volts×10^{-7})	R (e.m.u.)
1	18,600	33	38	−0.0079
1	−18,600	71		
2	18,600	− 25	72	−0.0075
2	−18,600	47		
4	18,600	−145	143	−0.0075
4	−18,600	− 2		
4	10,900	−123	90	−0.0080
4	−10,900	− 33		
4	3,370	− 92	28	−0.0081
4	3,370	− 64		
6	18,600	−264	217	−0.0076
6	−18,600	− 47		

The P.D. given in the table for each current is the average of several readings. The error is estimated to be less than 8 percent.

Hall e.m.f. as a function of crystal orientation

It has been pointed out by Wold[3] that for a metal whose crystal form is cubic one would expect the Hall coefficient to be independent of the orientation of the crystal axis. In connection with this, it seemed that if we should melt a sample with which we were working and allow it to cool slowly, the crystal orientation which it would assume would vary from one trial to the next, and if the Hall coefficient were a function of the crystal orientation, it would vary with successive meltings. Consequently some of the specimens were melted and carefully cooled several times, but in each case the same Hall constant was obtained. This, of course, is in accord with the fact that the Hall constant for the independent molds 3, 4 and 5, is nearly the same, since the chance for identical orientation of the crystals in the samples is very small. Whether, indeed, a definite crystal orientation throughout the specimen results when solidification takes place is purely speculative. However, the evidence points to the fact that the Hall coefficient for the alkali metals is independent of the crystal orientation in the strip, as would be expected for a cubic crystal lattice.

APPLICATION OF THE THEORY OF SOMMERFELD AND FRANK TO THE ALKALI METALS

According to the theory developed by Sommerfeld and Frank,[4] the Hall constant is given by $R=\rho C^{\frac{1}{2}}$, where ρ is the resistivity of the metal, and C a constant in the function which gives the fractional change in resistance of the metal in a magnetic field, *viz.*, $\Delta\rho/\rho=BH^2/(1+CH^2)$.

Kapitza[5] has studied the change in resistance for lithium and sodium, and though his data are incomplete, it is of some interest to investigate the order of magnitude of the Hall constant predicted by the theory mentioned above.

For lithium Kapitza's data give, $\Delta\rho/\rho=0.02$ when $H=90{,}000$ gauss. Consequently $B=2.47\times10^{-12}$ and $C=5.34\times10^{-12}$. Finally, then, $R=0.0030$, while the experimentally determined value is 0.0017.[1]

[3] P. I. Wold, Science **68**, 183 (1928).
[4] A. Sommerfeld and N. H. Frank, Rev. Mod. Phys. **3**, 1 (1931).
[5] P. Kapitza, Proc. Roy. Soc. **A123**, 292 (1929).

In the case of sodium, Kapitza has not obtained sufficient data for determining the constant B, since the change in resistance for the lower fields was too small to measure. However, he does give $\Delta\rho/\rho$ for 300,000 gauss. Now B for sodium will be smaller than for lithium, and if we assume $B=2.0$, we obtain $R=0.0042$, while the observed value is 0.0021. In fact, if we study the effect of varying B, we find that for $B=2.5$, $R=0.0049$; while for $B=1$, $R=0.0018$. It is evident, then, that for lithium and sodium, the value of the Hall constant predicted by the theory of Sommerfeld and Frank is certainly of the correct order of magnitude and that there is a possibility of close agreement when complete data are obtained. In the case of potassium and caesium, since no values are available for the change of conductivity in a magnetic field, the results of the above theory cannot be found.

In conclusion it is a pleasure to acknowledge our indebtedness to Professor P. I. Wold for many valuable suggestions, and for the facilities put at our disposal.

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Line Strengths in Intermediate Coupling

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The sum rules applicable to intermediate coupling are discussed in §1; in §2 proofs are given for two which are essentially new: the *J-file sum rule* which states that *for any coupling, in a transition array in which the jumping electron is not equivalent to any electron in the ion in either the initial or final configuration, the sum of the strengths of the lines originating in (or terminating on) a common level of quantum number J is proportional to 2J+1;* and the *J*-group-file sum rule which says that for any transition array of this type in which the valence electron jumps from *s* to *p* or *p* to *s*, the individual *J*-groups may be split up in one direction into invariant files. The dispersion measurements of Ladenburg and Levy on the neon transition array $2p^53p\rightarrow 2p^53s$ furnish in §3 an interesting experimental verification of these rules. The predictions of the usual first-order quantum-mechanical theory regarding the line strengths in this neon array are investigated in §4. It is concluded that this approximation does not enable the eigenfunctions to be determined with sufficient accuracy from the observed energy levels for quantitative intensity predictions.

§1. Sum Rules in Intermediate Coupling

THE sum rules which are applicable to a transition array in intermediate coupling will be made most clear if we prove them first for a particular array such as p^2s-p^2p (shown in Table I in *LS* coupling), and extend the proofs to more general arrays later.

All the sum rules apply to quantities of the type $S(\alpha J, \alpha' J')$, which we call the strength of the line from the level αJ to the level $\alpha' J'$, and which is defined as the sum $\Sigma_{M,M'}|(\alpha JM|\boldsymbol{P}|\alpha' J'M')|^2$ of the absolute squares of the components of electric moment. Under conditions of natural excitation the intensity of radiation of this line is given by

$$I(\alpha J\rightarrow\alpha' J') = N(\alpha J)\cdot 64\pi^4\nu^4 S(\alpha J, \alpha' J')/3c^3(2J+1),$$

where $N(\alpha J)$ is the number of atoms in the level αJ. The line strengths are usually expressed in the form[1]

$$S(\alpha J, \alpha' J') = (2J+1)\,|(\alpha J\,|P|\,\alpha' J')|^2\,\Xi(J, J'), \quad (1)$$

where

$$\Xi(J, J+1)=(J+1)(2J+3);\quad \Xi(J, J)=J(J+1);$$
$$\Xi(J, J-1)=J(2J-1).$$

The quantities $(\alpha J\,|P|\,\alpha' J')$ transform like the elements of the matrix of an observable in going

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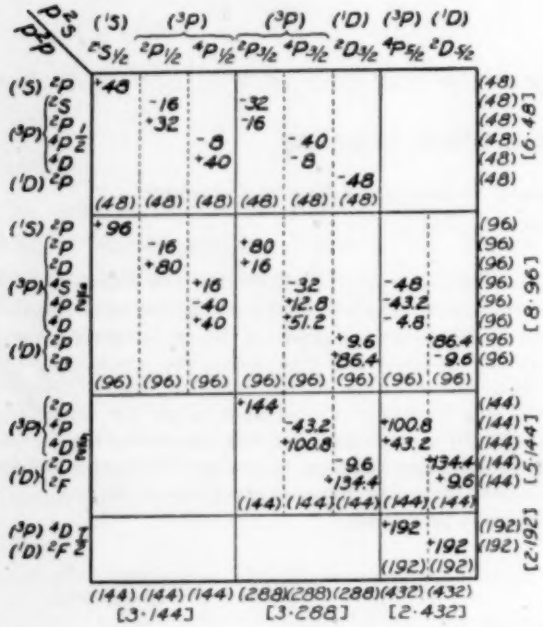
[1] See Born and Jordan, *Elementare Quantenmechanik*, p. 159, Eq. (10), or Güttinger and Pauli, Zeits. f. Physik 67, 754 (1931), Eq. (23).

TABLE I. *The transition array p^2p-p^2s in LS coupling as an illustration of the sum rules.* The individual columns and rows of this array are each *J files;* the fourth column (containing the entries 32, 16, 80, 16, 144) is the *J* file referring to the level $p^2\,(^3P)\,s\,^3P_{3/2}$; the third row (containing the entries 32, 16) is the *J* file referring to $p^2\,(^3P)\,p\,^3P_{1/2}$. The rectangles set off by solid lines, of which there are eight in which transitions are allowed by the selection rules, are each *J groups.* The rectangle at the top center of the array (containing the entries 32, 16, 40, 8, 48) is the *J* group labeled by $J=1\frac{1}{2}$ for p^2p and $J=\frac{3}{2}$ for p^2s. The broken lines break each *J group* up into two or three *J-group files;* the first file of the *J* group just mentioned contains the entries 32, 16; the second, 40, 8; the third the single entry 48.



from one coupling to another for a free atom. Hence the matrix of the quantities $S^{\frac{1}{2}}(\alpha J, \alpha' J')$, defined as the square roots of the strengths S taken + or − according to the sign of $(\alpha J \| P \| \alpha' J')$, transforms like the matrix of an observable since states of different J values do not become mixed up. These quantities $S^{\frac{1}{2}}(\alpha J, \alpha' J')$ are the most convenient to transform to intermediate coupling.

Table I gives, for *LS* coupling, the values of the line strengths S, and as superscripts the signs of $S^{\frac{1}{2}}$, for the transition array p^2s-p^2p (the line strengths are symmetric in the initial and final states).[2]

[2] Calculated by the method given in Johnson, Proc. Nat. Acad. Sci. **19**, 916 (1933) and Shortley, Proc. Nat. Acad. Sci. **20**, 591 (1934), for a particular choice of phases of the eigenstates.

In a transition array, the set of all lines originating in levels of one given J value and terminating on levels of a second given J value was called by Harrison and Johnson[3] a *J*-group. In Table I all boxes set off by solid lines are *J*-groups. The *J-group sum rule* which they proved states that *the strengths of the J-groups*[4] *are independent of coupling.* This follows immediately from the principle of spectroscopic stability *for any transition array whatsoever.*

In a transition array, the set of lines connecting a single given level of one configuration with all levels of the other configuration we shall call the *J-file* referring to that level. The different rows of Table I are *J*-files referring to the levels of p^2p, and the columns are *J*-files referring to the levels of p^2s. Now *in LS coupling* for a transition array in which the jumping electron is not equivalent to any in either ion, it follows from the known formulas for the relative strengths of the lines that the strengths of the different *J*-files referring to the levels of the same configuration are proportional to the values of $2J+1$ for those levels. Thus the strengths of the rows and columns, shown at the right and bottom of Table I, are separately proportional to $2J+1$. The same sum rule is known to hold for this same class of transition arrays in *jj* coupling. Hence it was immediately obvious from spectroscopic stability that the sum of the strengths of *all* the *J*-files of the array which refer to a given J value and a given configuration should be invariant and hence proportional to $(2J+1)$ times the number of such files, in any coupling.[5] These sums are shown in square brackets in Table I.

However Kronig,[6] in considering on the basis of the old quantum theory the old vector model in which configuration assignments were only made for the valence electron, states that the "intensities" of the *separate* *J*-files should be invariant. This statement seems not to have been repeated elsewhere nor to have been investigated quantum mechanically. Now if we examine the

[3] Harrison and Johnson, Phys. Rev. **38**, 757 (1931).

[4] By the strength of a set of lines we mean the sum of the strengths of the lines in the set.

[5] See, e.g., Pauling and Goudsmit, *Line Spectra*, p. 141.

[6] Kronig, Zeits. f. Physik **33**, 268 (1925).

matrix of S^1 for p^2p-p^2s (whose elements are the square roots of the strengths of Table I taken with the indicated signs) we note that any two rows or any two columns of S^1 headed by the same J value are orthogonal. This is sufficient to establish the invariance of the strengths of the separate files in this case, for if in any matrix the sum of the squares of the elements is the same for each row (or column) and the rows (columns) are orthogonal, these properties are independent[7] of unitary transformations of the states labeling the rows and of the states labeling the columns.

In fact, as we shall show in §2, in any case in which the strengths of the files are known to be proportional to $2J+1$ in LS coupling, they individually have the same values in all intermediate coupling. This theorem, which we shall call the *J-file sum rule* states that *for any coupling, in a transition array in which the jumping electron is not equivalent to any electron in the ion in either the initial or final configuration, the strengths of the J-files referring to the levels of the initial (final) configuration are proportional to the values of $2J+1$ for those levels.* In addition, for the particular two-electron arrays $nlnl''-nl^2$, the strengths of the J-files referring to nl^2 (but not those referring to $nln'l'$) are proportional to $2J+1$.

In the particular cases of the arrays $\alpha s-\alpha p$, in which the valence electron jumps from s to p or p to s and is not equivalent to any electron in the ion, we can further break the individual allowed J-groups up into invariant files referring to the levels of the configuration αs. These we shall call *J-group files. In such a transition array in any coupling the strength of a J-group file anywhere in the array is equal to the strength of a J-file referring to the J-value of the configuration αp which labels the J-group.* In Table I the J-group files are set off by broken and solid lines; their strengths (shown in parentheses) are equal to the strengths of the rows as given at the right of the table and are invariant since the different files in a J-group are obviously orthogonal. This *J-group-file sum rule* was recognized by Harrison and Johnson to hold in the particular case of two-electron transitions $ls-lp$. We shall sketch a general proof in §2.

A further illustration of these three sum rules is furnished by the strengths in Table IIa, b of p^5p-p^5s or $pp-ps$ in jj and LS coupling.

§2. Proof of the J-File and J-Group-File Sum Rules

In order to prove the invariance of the individual J-files it will be simplest to consider the scheme in which each electron is characterized by quantum numbers nlm_lm_s. Then if the valence electron is not equivalent to any in the ion in either the initial or final configuration, the matrix component of electric moment $\boldsymbol{P}$ vanishes unless all quantum numbers referring to the ion are the same in the initial and final states, in which case it equals the one-electron matrix component

$$(nlm_lm_s|\boldsymbol{P}|n'l'm_l'm_s')$$

if the valence electron initially has quantum numbers nlm_lm_s and finally quantum numbers $n'l'm_l'm_s'$.

Now from the dependence of this matrix component on m_l and m_l' as given by Born and Jordan[1] it follows that

$$\sum_{m_l'm_s'}(nlm_lm_s|\boldsymbol{P}|n'l'm_l'm_s')\cdot(n'l'm_l'm_s'|\boldsymbol{P}|nlm_l''m_s'')$$
$$=\delta(m_l,m_l'')\delta(m_s,m_s'')|(nl\,\vdots P\vdots\,n'l')|^2\Xi(l,l'). \quad (2)^8$$

Hence in this scheme the sum of the absolute squares of the matrix elements of $\boldsymbol{P}$ having a common original state is independent of that state, and the files of matrix elements from two original states have vanishing scalar product. A simple extension of the proof cited in reference 7 shows these properties to be invariant under unitary transformations, so that in any scheme labeled by JM, the lines having the initial state αJM have the strength sum $|(nl\,\vdots P\vdots\,n'l')|^2\,\Xi(l,l')$; hence the J-file referring to the initial level αJ has the strength

$$(2J+1)|(nl\,\vdots P\vdots\,n'l')|^2\,\Xi(l,l'). \quad (3)$$

Symmetrically, the J-file referring to the final level $\beta J'$ has the strength

$$(2J'+1)|(n'l'\,\vdots P\vdots\,nl)|^2\,\Xi(l',l). \quad (4)$$

[7] This is proved in Eq. (9) of Harrison and Johnson (reference 3).

[8] $(n,l\,\vdots P\vdots\,n',l-1)=-e(4l^2-1)^{-\frac{1}{2}}\int_0^\infty rR(n,l)R(n',l-1)dr.$

These equations show that rows and columns of a transition array labeled by the same J value have relative strengths $\Xi(l, l')/\Xi(l', l)$. This ratio $\Xi(p, s)/\Xi(s, p)=1/3$ is seen to obtain in Tables I and II.

The applicability of the J-file sum rule to the files referring to nl^2 in the array $nl^2 \rightarrow nln'l'$ arises from the fact that the strengths of the allowed lines in this array are just twice those of the corresponding lines of $nln''l \rightarrow nln'l'$,[9] and that none of the lines in the nl^2 files are forbidden.

This completes the proof of the J-file sum rule.

The J-group-file sum rule states that for the transition array $\alpha s \rightarrow \alpha p$ in any coupling characterized by J values, the sum of the strengths of all lines in the J-group $J \rightarrow J'$ having a common level of the configuration αs equals $(2J'+1)\,|(p\,\|P\|\,s)|^2\,\Xi(p, s)$. The quantum numbers which characterize the levels in jj coupling are a set I referring to the ion, nsj or $n'pj'$ for the valence electron, and the resultant J value. In jj coupling two files in the same J-group are obviously orthogonal since they refer to different ionic quantum numbers I. The strength of a J-group file is $\Sigma_{j'} S(I, nsj, J; I, n'pj', J')$ where $j=1/2$ and $j'=1/2, 3/2$. This sum may without difficulty be evaluated directly from formulas given by Güttinger and Pauli[1] for the three special cases $J'=J+1$, J, and $J-1$, and shown to have the value stated in the theorem.

§3. Application to the Neon Red-Yellow Lines

The neon transition array $2p^5 3p \rightarrow 2p^5 3s$, which, with the old intensity measurements of Dorgelo, has been used to infer that the J-file sum rule should not hold in intermediate coupling, will, with the new dispersion measurements of Ladenburg and Levy,[10] furnish us with instead a very interesting experimental verification.

The relative line strengths calculated from the Einstein A values of L. and L. by the relation $S(p, s)=3hc^3(2J_p+1)\,A(p, s)/64\pi^4\nu^3$ are given in Table IIc.[11] The ratios of the sums which should be invariant to their values in IIa and IIb are shown in parentheses. To the first order of the perturbation theory, which is expected to be rather good in this particular case, these ratios should all be equal.

Now the relative strengths of lines having a given final level were obtained by L. and L. by measurements of anomalous dispersion to an accuracy of perhaps 10 percent, while the strengths in different rows of the diagram were only related by direct measurements of much less accuracy of relative intensity of lines having the same initial level. This suggests that we try relating the strengths in the different rows by requiring the J-file sum rule to hold exactly with respect to the rows; this amounts to discarding the direct intensity measurements and using only the dispersion measurements. Such a procedure seems further justified by the fact that the ratios for the three J-group files in each row are of approximately the same size but that these ratios differ much between rows; there is a real discrepancy in the first row for which we have no explanation. The test of this procedure will come from an examination of the sums of the columns in the modified array, for one would not in general expect an improvement in these sums upon multiplication of the rows by arbitrary factors.

Table IId shows the array modified so that the sums of the rows have exactly the theoretical relative values, and it is seen that there is a great improvement in the ratios of the sums of the columns to their theoretical values. In fact, this agreement becomes almost as good as one could expect from the accuracy of the data.

§4. Direct Quantum-Mechanical Calculations

While considering neon $2p^5 3p \rightarrow 2p^5 3s$, it seems of interest to see what the first-order perturbation theory has to say about the detailed line-strength pattern when we use only the ordinary electrostatic and spin-orbit interaction terms and evaluate the coupling constants (radial integrals) from the observed energy values. In order to do this, we first calculate the transformations from LS coupling to the actual coupling for $p^5 s$ and $p^5 p$, and then transform the matrix of S^1 from LS coupling to the actual coupling.

[9] Shortley, Phys. Rev. **40**, 185 (1932), §8.

[10] Ladenburg and Levy, Zeits. f. Physik **88**, 461 (1934).

[11] The notation of Bacher and Goudsmit is used for the levels of $p^5 p$. The three bracketed values in this table are very rough estimates, from the measurements of Dorgelo, of the strengths of lines which were not measured by L. and L. The designation v.s. means 'very small.'

TABLE II. *Line strengths in the transition array $2p^53p-2p^53s$.* In a and b, the sums in parentheses are predicted to be independent of coupling. The ratios of the actual sums in c and d to these predicted sums are shown in parentheses in c and d.

a: jj Coupling

	$\frac{1}{2}\frac{1}{2}0$	$\frac{1}{2}\frac{1}{2}0$	$\frac{1}{2}\frac{3}{2}1$	$\frac{3}{2}\frac{3}{2}1$	$\frac{1}{2}\frac{1}{2}1$	$\frac{3}{2}\frac{1}{2}1$	$\frac{3}{2}\frac{3}{2}2$	$\frac{3}{2}\frac{1}{2}2$	$\frac{1}{2}\frac{3}{2}2$	$\frac{3}{2}\frac{3}{2}3$	
$\frac{3}{2}\frac{1}{2}2$				-5		-25 (30)	+25	+25 (50)		+70 (70)	(150)
$\frac{1}{2}\frac{1}{2}1$	-10 (10)		+10		+20 (30)			+50 (50)			(90)
$\frac{3}{2}\frac{1}{2}1$	-10 (10)			+25		-5 (30)	+25	-25 (50)			(90)
$\frac{1}{2}\frac{1}{2}0$			+20		-10 (30)						(30)
	(10)	(10)	(30)	(30)	(30)	(30)	(50)	(50)	(50)	(70)	

b: LS Coupling

	$^1S_0$	$^3P_0$	$^3P_1$	$^1P_1$	$^3D_1$	$^3S_1$	$^3P_2$	$^1D_2$	$^3D_2$	$^3D_3$	
$^3P_2$			-12.5		$-\frac{5}{6}$ (30)	$-16\frac{2}{3}$	+37.5	+12.5 (50)		+70 (70)	(150)
$^3P_1$	-10 (10)		+7.5		+12.5 (30)	-10	-12.5	+37.5 (50)			(90)
$^1P_1$	-10 (10)			+30		(30)		+50 (50)			(90)
$^3P_0$			-10		$+16\frac{2}{3}+3\frac{1}{3}$ (30)						(30)
	(10)	(10)	(30)	(30)	(30)	(30)	(50)	(50)	(50)	(70)	

c: Ladenburg & Levy

	10_0	6_0	9_1	7_1	4_1	1_1	8_2	5_2	3_2	2_3	
$^3P_2'$			6.5	-2.9	5.4	16.9 (1.06)	8.9	18.9	13.2 (.82)	53.1 (.76)	.84
$^3P_1'$	v.s.	8.7 (.87)	-3.9	[.1]	16.3	10.3 (1.02)	13.4	5.8	23.5 (.85)		.91
$^1P_1'$	12.8	v.s. (1.28)	18.6	19.0	v.s.	[3.0] (1.35)	30.6	29.6	7.4 (1.35)		1.34
$^3P_0'$			8.6	14.5	9.0	[1.0] (1.10)					1.10
	(1.28	.87	1.26	1.22	1.02	1.04	1.06	1.09	.88	.76)	

d: L. & L. Modified

			7.7	-3.4	6.5	20.2 (1.26)	10.7	22.5	15.7 (.98)	63.3 (.90)	(.001
v.s.	9.6 (.96)		-4.3	[.1]	17.9	11.3 (1.12)	14.7	6.3	25.8 (.94)		.001
9.6	v.s. (.96)		13.9	14.1	v.s.	[2.2] (1.01)	22.7	22.0	5.5 (1.00)		.001
			7.8	13.2	8.1	[.9] (1.00)					.001)
(.96	.96		1.12	1.03	1.08	1.15	96	1.02	.92	.90)	

e: Calculation A

		5.7	2.5	2.4	19.5	16.9	16.6	16.5	70.0
.2	9.8	6.2	.1	15.5	8.2	24.0	0.0	26.0	
9.8	.2	10.0	18.0	1.9	.1	9.1	33.4	7.5	
		8.1	9.4	10.2	2.3				

f: Calculation B

		6.1	2.8	2.2	18.9	21.3	13.8	14.9	70.0
.2	9.8	2.6	2.4	16.5	8.5	15.2	1.4	33.5	
9.8	.2	13.7	16.0	.1	.2	13.5	34.9	1.6	
		7.5	8.9	11.2	2.4				

Neon $2p^53s$ fits Houston's formulas almost perfectly, giving for the eigenstates in the actual coupling

$$\psi(^1P_1')=0.964\psi(^1P_1)+0.266\psi(^3P_1)$$
$$\psi(^3P_1')=0.266\psi(^1P_1)-0.964\psi(^3P_1). \quad (5)$$

The agreement with the observed energy levels and Zeeman effect is so good that the error in these transformation coefficients is probably not more than 0.001.[12]

The situation with respect to $2p^53p$ is unfortunately not so attractive. We use the electrostatic interactions in *LS* coupling as given in §4 of reference 9. The spin-orbit interaction is obtained from Johnson's[13] matrix for pp by writing $-\zeta_{2p}$ for a_1 and ζ_{2p} for a_2, where the ζ's are the (essentially positive) integrals expressing the spin-orbit interaction of one electron in a central field. Inglis and Ginsburg found a fairly good agreement with the observed energy levels by use of the constants given under A in Table

TABLE III.

	Calc. A	Calc. B		Calc. A	Calc. B
F_0	−339.1	−334.9	$12G_2$	537	482.8
F_2	157.7	166.6	ζ_{3p}	402.8	385.6
$6G_0$	4503	4604.5	ζ_{2p}	40.0	−8.4

[12] This enables us to predict the relative intensity of the two resonance lines of neon as $(^1P_1'\rightarrow{}^1S_0)/(^3P_1'\rightarrow{}^1S_0)=13.2$ with an estimated error of about 0.1.

[13] Johnson, Phys. Rev. **38**, 1628 (1931). Note that a_1+a_2 should be written in place of a_1-a_2 in the matrix for $J=0$, as pointed out by Inglis and Ginsburg.

TABLE IV.

	Energy (cm^{-1})			g value		
	obs.	A	B	obs.	A	B
$2_3\ ^3D_3$	0.0	0.0	− 28.7	1.329	1.333	1.333
$3_2\ ^3D_2$	167.2	127.7	149.2	1.137	1.147	1.146
$5_2\ ^1D_2$	658.8	728.6	667.8	1.229	1.142	1.106
$8_2\ ^3P_2$	1201.5	1171.2	1170.1	1.301	1.377	1.415
$1_1\ ^3S_1$	−1399.2	−1271.4	−1358.1	1.984	1.994	1.993
$4_1\ ^3D_1$	464.6	378.2	394.5	.669	.574	.561
$7_1\ ^1P_1$	1115.1	1085.3	1144.1	.999	1.095	1.105
$9_1\ ^3P_1$	1381.4	1369.7	1386.3	1.340	1.340	1.339
$6_0\ ^3P_0$	1260.4	1276.0	1325.0			
$10_0\ ^1S_0$	3313.7	3298.3	3313.2			

III.[14] These constants lead to the energy levels and g values listed under A in Table IV. The matrix which expresses these levels in the LS-coupling scheme is easily obtained; the Russell-Saunders level which occurs in largest proportion in each of these levels is listed in Table IV.[15]

The signs in the matrix of S^1 in Table IIb were obtained for states having the same phases as in the energy matrix we have used for p^5p and in (5). When we transform this matrix to the actual coupling of calculation A we obtain the line strengths of Table IIe, which show the general characteristics of the departures of the observed values from those in Russell-Saunders coupling, but disagree markedly in detail.

In order to see whether this disagreement is of the right order of magnitude to be accounted for by the fact that with our approximate formulas we could not fit the observed energy levels perfectly, we have in calculation B used a set of constants chosen so as to give approximately the best least-squares fit of the calculated to the observed energies.[16] These constants give the energies listed in Table IV (B), which, while they fit better on the average, are not a great improvement over those of calculation A. The small shifts between A and B change the differences between energy levels of the same J value considerably, and this and the change in the constants change the eigenfunctions sufficiently to give the line strengths of Table IIf instead of IIe. The marked differences between these tables shows that we cannot expect, without further refinements in the theory, to get accurate quantitative intensity predictions in this case. The same observation with respect to g values has been made by Inglis and Ginsburg.

I wish here to express to Professors Harrison and Van Vleck and Dr. Kimball my appreciation for valuable discussions and suggestions concerning this work, and to thank Professor Ladenburg for calling my attention to his neon dispersion data before publication.

[14] Inglis and Ginsburg, Phys. Rev. **43**, 194 (1933). We find that the calculated energies given by Inglis and Ginsburg are not correct for the parameters they list. This statement is easily checked by an evaluation of the trace of say the $J=2$ matrix. The sum of the observed energies of the three levels of $J=2$ is 2027.5 cm^{-1}, the sum of their calculated energies 2058.5. Now the trace of the energy matrix is, in their notation, $\alpha+\gamma-\frac{3}{2}(a_1+a_2)=2027.5$—in agreement with the observed trace but not with their calculated trace as it should be. This discrepancy is entirely accounted for by an error of about 30 cm^{-1} in their value 1201.5 for the level 8_2. Similarly, we find their calculations for the levels of $J=1$ and 0 to be all in error by amounts ranging from 6 to 56 cm^{-1}. These discrepancies account for the difference between the energies and g values in Table IV (A) and those given by Inglis and Ginsburg.

[15] These proportions run from 60% for 7_1 (7_1 is 60% $^1P_1$, 29% $^3P_1$, 11% $^3D_1$, 0% $^3S_1$—in calculation B these proportions become 61%, 30%, 9% and 0%) to 100% for 2_3; on the average the levels contain 85% of the Russell-Saunders level indicated. In Tables IIc, d, e, f, these levels occupy the same columns as the corresponding Russell-Saunders levels in Table IIb.

[16] This we may do in the following way. The energy levels $\lambda_1\cdots\lambda_{10}$ are the roots of four polynomials whose coefficients $c_1\cdots c_{10}$ are functions of six parameters $F_1\cdots F_6$. We know $\partial c_k/\partial F_j$ and $\partial\lambda_i/\partial c_k$. (We have not succeeded in finding a reference to the formula for the rate of change of a root of a polynomial with respect to a coefficient, so we state the general formula here: If the nth degree equation $\lambda^n+\sum_{i=0}^{n-1}c_i\lambda^i=0$ has roots $\lambda_1\cdots\lambda_n$, then

$$\partial\lambda_1/\partial c_j=-\lambda_1{}^j/\prod_{i=2}^{n}(\lambda_1-\lambda_i),$$

where λ_1 is any one of the roots.) From these we obtain $\partial\lambda_i/\partial F_j$. Now, knowing an approximate set $(F_1\cdots F_6;\ \lambda_1'\cdots\lambda_{10}')$ of parameters and energy levels, we write $\lambda_i{}^\circ-\lambda_i'=\sum_j(\partial\lambda_i'/\partial F_j)\delta F_j$, where the $\lambda_i{}^\circ$ are the observed energies, and determine the six δF_j by a least-squares calculation to fit these equations as well as possible. Since the dependence of the roots on the parameters is only to a first approximation linear, this process may be repeated for greater accuracy. However in our case the dependence was sufficiently linear that there was no point in doing more than one calculation of this sort in getting from A to B.

Mean Kinetic Energy and Mean Energy Spent in Excitation by Electrons Drifting Through Dense Gases

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Two fundamental equations are used to calculate the mean kinetic energy and mean energy spent in excitation by electrons drifting through dense gases. The first equation is a statement of some of the energy relations in the passage of an electron avalanche from the cathode to the anode, and the second equation is an evaluation of the mean kinetic energy of the drifting electrons from some of the experimental data on the probability of ionization. The average energy lost by an electron per collision in exciting any level or levels of a gas molecule can be calculated from the two fundamental equations. For ratios of E/p (field strength in volts per cm to pressure of the gas in mm of mercury) from 39 to 1000, the mean kinetic energy of the electrons drifting through nitrogen gas was found to vary approximately linearly from 3.42 to 35.6 equivalent volts. The mean energy spent in excitation per collision rose to 8.8 equivalent volts for a mean kinetic energy of 35.6 equivalent volts.

I. INTRODUCTION

SINCE the phenomena involved in the calculations are somewhat complicated it is thought best at the outset to state formally just what it is desired to find. The object of this paper is as follows:

First, to develop a general method for calculating the mean kinetic energy of the electrons drifting through a relatively dense gas of known pressure under the influence of a given electric field.

Second, to utilize the calculated values of the mean kinetic energy of the drifting electrons to find the mean energy spent by an electron per collision in exciting one or more of the energy levels of a molecule or atom of the given gas.

Third, to discuss the significance of the results obtained, e.g., to find what other physical values or coefficients can be obtained from a knowledge of the mean kinetic energy of the drifting electrons, and whether the relatively large values of the energy spent in excitation per collision for electron energies many times greater than the ionizing potential support the evidence[1] that many energy levels have second maxima for the probabilities of excitation.

The electron mobility, the probability of ionization and of excitation, the angle of scattering, the coefficient of recombination and a number of secondary effects are functions of the mean kinetic energy of the drifting electrons. Of these phenomena, the probability of ionization is perhaps best known as a function of the kinetic energy of the colliding electrons under conditions such that secondary effects are practically eliminated. We use this information to get a relation between the mean kinetic energy, the average energy spent per collision in excitation and the ratio E/p (field strength in volts per cm to pressure in mm of mercury) in a discharge of the Townsend type. In discharges of this type with very low current density, secondary effects such as ionization and excitation by successive electron impacts, collisions of the second kind, effects of metastable atoms, etc., are practically eliminated, and the ionization and excitation produced are approximately independent functions of the gas pressure and the electron kinetic energy.

In any similar low current density experiment, the value of the average electron speed will be given in terms of E/p and from this speed the electron mobility, scattering and diffusion may be evaluated. The data can of course not be applied to high current density discharges in which secondary effects such as ionization and excitation by successive impacts occur.

Each energy level has a certain likelihood or probability of excitation per electron collision, but this probability of excitation is known for only certain energy levels of a few atoms and molecules. Because of the great labor involved in measuring the likelihood of excitation for each energy level of the molecule, a method for giving a measure of the composite or total excitation probability for all the energy levels of a molecule

[1] J. J. Thomson and J. P. Thomson, *Conduction of Electricity through Gases*, Vol. II, p. 108.

would seem to be of interest. The quantity calculated is the average energy spent in excitation per electron collision. This given quantity we will designate by $\bar{V}_e$. The experiments of Renninger,[2] Jones and Whiddington,[3] Hughes and McMillen,[4] and the calculations of Massey and Mohr,[5] seem to indicate such a large value for the probability of excitation as compared with the direct determinations of particular energy levels by Sponer,[6] Eldridge,[7] Brattain,[8] Dymond,[9] and Glockler,[10] at relatively low electron energies as to warrant the suggestion[1] that in many cases the excitation probability for an energy level rises to a second maximum for electron energies large relative to the ionizing potential.

Atkinson[11] has calculated a function somewhat similar to the mean energy spent in excitation per collision. He found the total probability for the occurrence of an inelastic impact for idealized conditions in neon, and obtained a value of about 5 percent when E/p was 13. The purpose of the present paper is to calculate the mean kinetic energy of the drifting electrons, and the average energy spent in excitation per electron impact, but by a method different from that of Atkinson for the total probability of excitation, and for a considerable range in values of E/p.

II. Method of Calculation

In an experiment for measuring the amount of ionization by collision, e.g., as performed by one of the Townsend school,[12] let an electron avalanche start as a single electron from the cathode and grow in size until it reaches the anode. (The term "electron avalanche" in English corresponds to "Elektronenlawine" in German. It refers to the cumulative growth of a cloud of electrons in their passage from cathode to anode as caused by ionization by collision.)

In such experiments the current flowing between the cathode and anode may be measured by an electrometer, and is of the order of 10^{-8} amp. or less, and secondary effects such as ionization of excited atoms, collisions of the second kind, and the action of metastable atoms can be neglected for pure gases.[13] In the range for which the equation will be developed, the ratios of E/p (from 30 to 1000 volts per cm per mm of mercury) are sufficiently large so that diffusion gradients and space charge play a minor role. The value of x is taken large enough so that small irregularities near the cathode are smoothed out and the experimental relation $N=N_0\epsilon^{\beta x}$ for ionization by collision is satisfied, where N is the number of ion pairs produced by N_0 initial electrons leaving the cathode and traveling x cm in the direction of the field, and β is the number of ions produced by one electron per cm of path in the direction of the field. The average kinetic energy of the electron avalanche is assumed at this distance to be independent of x, for the amount of ionization by collision is a function of the mean kinetic energy of the electrons, and if this energy varied with x, the number of ion pairs produced per electron per cm would not be constant, and the experimental relation $N=N_0\epsilon^{\beta x}$ would not be satisfied. An approximate Maxwellian distribution is assumed. Pidduck[14] has shown that electrons drifting through a gas under the influence of an electric field and suffering elastic collisions only, would have a Maxwellian distribution. The work of Killian[15] with probe measurements on mercury vapor plasma indicates a Maxwellian distribution of electron velocities. Discharge conditions in a plasma are however different from those considered here.

Under these conditions, for each initial electron leaving the cathode, we have the following relations for the electron avalanche produced:

[2] Renninger, Ann.. d. Physik **9**, 295 (1931); **10**, 111 (1931).
[3] Jones and Whiddington, Phil. Mag. **6**, 889 (1928).
[4] Hughes and McMillen, Phys. Rev. **39**, 585 (1932).
[5] Massey and Mohr, Proc. Roy. Soc. **A132**, 605 (1931).
[6] H. Sponer, Zeits. f. Physik **7**, 185 (1921).
[7] J. A. Eldridge, Phys. Rev. **20**, 456 (1922); **23**, 685 (1928).
[8] W. H. Brattain, Phys. Rev. **33**, 474 (1929).
[9] E. G. Dymond, Proc. Roy. Soc. **A109**, 291 (1925).
[10] G. Glockler, Phys. Rev. **33**, 175 (1929).
[11] R. d'E Atkinson, Proc. Roy. Soc. **A119**, 335 (1928).
[12] Townsend school, Phil. Mag. [6] **3**, 557 (1902); **5**, 389 (1903); **6**, 598 (1903); **8**, 738 (1904); **11**, 535 (1906).
[13] Traces of impurity would produce a small error in β because of the action of collisions of the second kind and metastable atoms, but the error would be of the order of magnitude of the impurity.
[14] F. B. Pidduck, Proc. Roy. Soc. **A88**, 296 (1913).
[15] T. J. Killian, Phys. Rev. **35**, 1238 (1930).

Energy acquired from field in dx = Energy lost in ionization and excitation of molecules in dx + gain of kinetic energy in dx, or,

$$Ee\epsilon^{\beta x}dx = V_i\beta\epsilon^{\beta x}dx + \int_0^\infty N_{dc}\,(cdx/lu) \quad \bar{V}_e \quad + \beta\epsilon^{\beta x}dx\; 1.5\, m\alpha^2/2,$$

From field	Lost by ionization[16]	No. of electrons having speed dc	Collisions in dx of electrons having speed c	Average excitation energy per collision	Gain in kinetic energy of electrons in dx

where, E = the field strength in volts per cm, e = the electronic charge, β = the number of ion pairs produced per electron per cm of path in the direction of the field, x = number of cm from cathode, c = electron velocity in cm per sec., l = mean free path of the electron in cm, u = drift speed in cm per sec., α = most probable velocity in a Maxwellian distribution function, V_i = ionization potential, $\bar{V}_e$ = average excitation energy per collision.

Substituting for the drift speed,[18]

$$u = 0.85eEl/[2/(\pi)^{\frac{1}{2}}]m\alpha,$$

writing for N_{dc} the Maxwellian distribution and dividing by $\epsilon^{\beta x}dx$ we obtain

$$Ee = V_i\beta + \frac{8m\bar{V}_e}{0.85\pi eEl^2}\int_0^\infty \frac{c^3}{\alpha^2}\epsilon^{-c^2/\alpha^2}dc + 0.75\beta m\alpha^2. \tag{1}$$

A second equation is

$$\begin{Bmatrix}\text{No. of ions}\\ \text{formed in } dx\\ \text{at } x\end{Bmatrix} = \int_0^\infty \begin{Bmatrix}\text{No. of electrons}\\ \text{having speed } c\\ \text{in } dx\end{Bmatrix} \times \begin{Bmatrix}\text{No. of collisions of an}\\ \text{electron having the}\\ \text{speed } c \text{ in } dx\end{Bmatrix} \times \begin{Bmatrix}\text{Probability of ionization}\\ \text{per collision of an elec-}\\ \text{tron having speed } c\end{Bmatrix}$$

or,
$$\beta\epsilon^{\beta x}dx = \int_0^\infty \left(\frac{4\epsilon^{\beta x}}{(\pi)^{\frac{1}{2}}}\frac{c^2}{\alpha^3}\epsilon^{-c^2/\alpha^2}dc\right) \times \left(\frac{2cdxm\alpha}{0.85l^2eE(\pi)^{\frac{1}{2}}}\right) \times P'$$

or,
$$\beta = \frac{8m}{0.85\pi l^2eE}\int_0^\infty P'\frac{c^3}{\alpha^2}\epsilon^{-c^2/\alpha^2}dc. \tag{2}$$

P' is plotted against electron speed (using the data of Tate and Smith[19]), and a graphical solution of Eq. (2) is obtained. By trial that value of α is found which gives the experimental value of β. When this value of α is substituted in Eq. (1), $\bar{V}_e$ may be solved for.

III. Results

The results calculated by the above method for nitrogen and hydrogen are given in Table I and

[16] At higher electron velocities an electron may lose more energy in a collision than the ionizing potential, i.e., some of its energy may go into the kinetic energy of the ejected electron. This need not concern us here, however, for under the conditions assumed the average electron energy remains constant, and regardless of energy exchanges between electrons and electrons, and electrons and atoms, the only net change in the kinetic energy of the electron avalanche will be that required to raise the kinetic energy of the ejected electrons from zero to the average value of the electrons of the avalanche. Also in some cases part of the energy lost by an electron in an ionizing collision might be expected to go into the kinetic energy of dissociated molecules. The work of Smyth (reference 17) however, shows that there is no evidence for simultaneous ionization and dissociation in hydrogen, and that dissociation is a secondary reaction of the hydrogen ion, the required energy for dissociation and the energy of the ions coming from the initial work of ionizing the molecule.

[17] H. D. Smyth, Phys. Rev. **25**, 452 (1925).

[18] Lorentz, *Theory of Electrons*, Appendix p. 266; or Darrow, *Electrical Phenomena in Gases*, p. 176.

[19] Tate and Smith, Phys. Rev. **39**, 270 (1932).

TABLE I. *Calculated results for the mean kinetic energy and the mean energy spent in excitation per collision for nitrogen and hydrogen.*[20]

The symbols have the following meaning:
E/p—Ratio of the field strength in volts per cm to the pressure in mm of mercury.
β/p—A measure of the ionizing efficiency, where β is the number of ion pairs produced per electron per cm of path in the direction of the field, and p is the pressure in mm of mercury.
a^2—The square of the most probable electron velocity in cm/sec.
$\bar{V}=1.5ma^2/2$—The mean kinetic energy of the electrons in the electron avalanche in equivalent volts.
$\bar{V}_e$—The average energy spent in excitation per electron impact in equivalent volts.

E/p	β/p	$a^2\times10^{-18}$	$\bar{V}=1.5ma^2/2$	$\bar{V}_e$	E/p	β/p	$a^2\times10^{-18}$	$\bar{V}=1.5ma^2/2$	$\bar{V}_e$
Nitrogen					Hydrogen				
39.2	*0.013*	0.0808	3.42	0.302	30	0.08	1.05	4.47	0.548
100	0.42	1.51	6.36	0.967	50	0.36	1.50	6.35	0.944
300	3.90	3.26	13.8	2.72	100	1.37	2.40	10.2	1.82
500	6.20	4.80	20.2	4.62	200	2.8	4.20	17.8	3.41
700	*8.70*	6.30	26.6	5.99	300	3.6	5.45	23.1	5.95
900	*10.0*	7.71	32.7	7.80	400	(4.1)	6.60	28.0	9.00
1000	*10.5*	8.41	35.6	8.80	600	(4.6)	9.15	38.8	15.4
					800	(4.8)	11.8	50.1	22.1
					1000	(5.0)	15.2	64.5	26.6
					1200	5.1	19.1	81.0	30.0

plotted in Fig. 1. The data of Townsend[21] and Paavola[22] were used for the experimental values of β/p for nitrogen. To extend the calculations for nitrogen over a wider range in E/p, the values of β/p in italics were taken from the data for air although the experimental probability of ionization for nitrogen was used. The properties of the oxygen and hydrogen molecules are sufficiently close together so that no break is noticeable in the plotted curves at the junction between the values for nitrogen and those for air. The values of β/p for hydrogen were taken from other data of Townsend.[23] The numbers and points in the brackets are extrapolated values taken from a curve drawn through the plotted experimental points of the graph of β/p against E/p.

The kinetic theory values[24] of the electronic mean free path were used, i.e., at 0°C and a pressure of 1 mm of mercury the values of mean free path were $l=0.0755$ cm for hydrogen and $l=0.0359$ cm for nitrogen.

The initial values of β/p did not warrant an accuracy in the numerical calculations of $\bar{V}_e$ to less than three percent error.

The calculated values of the average kinetic energy of the electrons, $\bar{V}$, vary for nitrogen in an approximately linear manner with E/p in the range from 39 to 1000. For hydrogen however, the graph of $\bar{V}$ is definitely non-linear.

The values of $\bar{V}_e$ for both nitrogen and hydrogen increase with larger values of E/p, and in the case of hydrogen seem to be approaching a maximum at $E/p=1200$.

IV. Discussion of Results

The graphs in Fig. 1 illustrate the fact that the energies spent in ionization, excitation and the kinetic energy of the electrons are mutually dependent. If one variable has a linear relation with E/p over a certain range, then all three graphs have an approximately constant slope, but if one variable starts to change at a different rate, $\bar{V}$ also changes at a different rate, and hence the slope of the third graph changes, since it is also a function of $\bar{V}$.

The magnitudes of $\bar{V}_e$ are unexpectedly high, e.g., $\bar{V}_e=8.80$ for $\bar{V}=35.6$ equivalent volts in nitrogen, and $\bar{V}_e=30.0$ for $\bar{V}=81$ equivalent volts in hydrogen. There is considerable other evidence for such high values.

Massey and Mohr[26] made use of a theory of Oppenheimer's for interchange between the free electrons and those of an atom, and found the maximum calculated probability to be of the order of unity for the lowest critical level of helium, but much less than that for the levels giving rise to lines in the visible.

Hughes and McMillen[27] found that for electrons of from 40 to 200 volts energy, scattered

[20] Calculations were carried out to a higher degree of accuracy than that of the initial data in order to prevent cumulative error.

[21] Townsend, *Electricity in Gases*, p. 281.

[22] Paavola, Archive für Elektrotechnik **22**, 457 (1929).

[23] J. S. Townsend, Phil. Mag. [6] **5**, 389 (1903).

[24] No experimental values for the electronic mean free path for drift speed are known for the given electron energy region in which both ionization and excitation occur. It is interesting to note that in calculations carried out for $\bar{V}_e$ for hydrogen with an assumed value of mean free path 100 percent greater than the kinetic theory value, the magnitude of the maximum was decreased, but occurred for approximately the same value of the electron mean kinetic energy, $\bar{V}$, as occurred when the kinetic theory value of mean free path was used. The kinetic theory value of the electronic mean free path was taken as $l=4\sqrt{2}\lambda$, where λ is the mean free path of the molecules of hydrogen or nitrogen. The values of λ were calculated from an appendix given by Loeb[25] for the radii of the molecules as determined by viscosity measurements.

[25] L. B. Loeb, *Kinetic Theory of Gases*, Appendix I, p. 527.

[26] Massey and Mohr, Proc. Roy. Soc. **A132**, 605 (1931).

[27] Hughes and McMillen, Phys. Rev. **39**, 585 (1932).

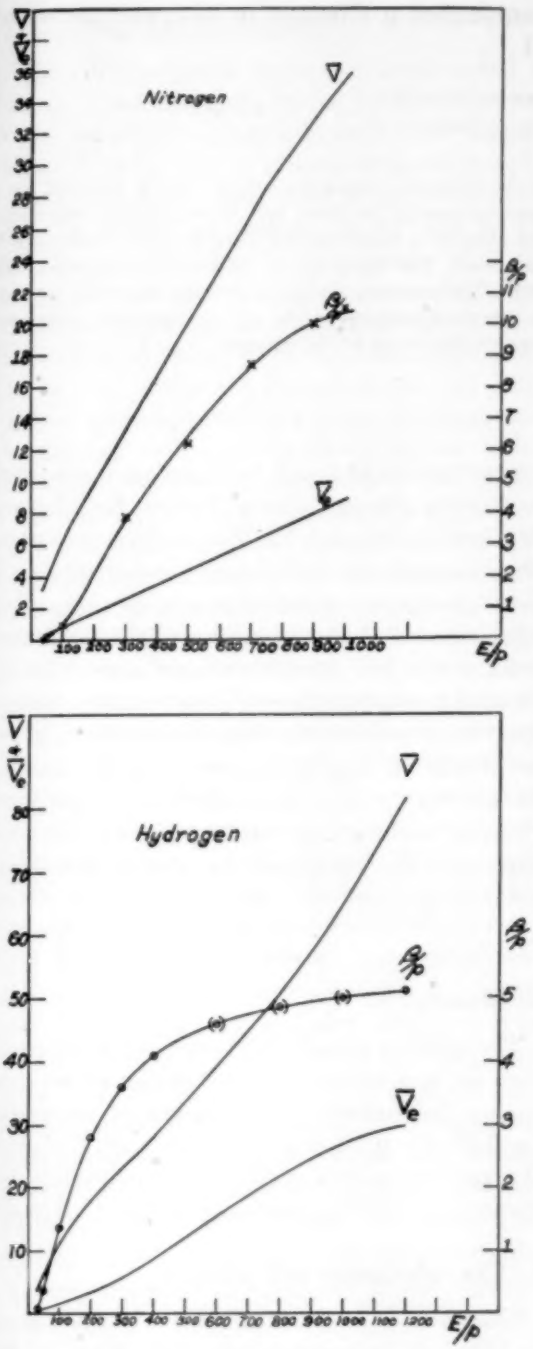

FIG. 1. Variation in electron ionizing ability β/p, the mean kinetic energy of the electrons $\overline{V}$, and the mean energy spent in excitation per collision $\overline{V}_e$, with E/p the ratio of the field strength to pressure. β/p is expressed in number of positive ions produced by one electron per cm of path per mm of mercury, $\overline{V}$ and $\overline{V}_e$ in equivalent volts, and E/p in volts per cm per mm of mercury.

in argon at an angle of 10 degrees, the likelihood of the 11.6 volt energy loss is comparable to that for ionization.

Two experimental methods may be used in measuring the variation in the probability of excitation of an energy level with the electron energy. The direct method utilizes a modification of the inelastic impact method, and the indirect method makes use of the likelihood of stimulation of the spectrum lines as measured by the photoelectric cell. By the direct method the curves for the probability of excitation against electron energy show sharp peaks close to the energy levels in question, but by the indirect method, although the triplet lines are similarly sharp, the singlet lines have rather broad and flat maxima occurring a few volts or tens of volts above the given energy level.[28] From these data one would expect $\overline{V}_e$, the mean energy spent in excitation per collision, to decrease for electron energies large with respect to the ionizing potential, since for nearly all energy levels the likelihood of excitation has begun to decrease for electron energies as high as 81 equivalent volts.[29] The results show, however, that $\overline{V}_e$ keeps increasing with the mean electron energy up to $\overline{V}=35.6$ volts for nitrogen and $\overline{V}=81$ volts for hydrogen.

These results indicate that the maximum likelihoods of excitation for at least some of the energy levels of the nitrogen and hydrogen molecules must rise to maxima for electrons with energies above 35.6 and 81 equivalent volts, respectively, as suggested by the Thomsons.[1]

The value of $\overline{V}_e=30$ equivalent volts for hydrogen shows that simultaneous excitation of a number of energy levels of the hydrogen molecule occurs for electrons with energies a few times that of the ionizing potential.

I wish to express my appreciation for the interest and suggestions of Dr. K. K. Darrow who so kindly pointed out many significant features of the above problem.

[28] Darrow, *Electrical Phenomena in Gases*, p. 100.

[29] For high electron energies simultaneous ionization and excitation may be produced in one collision by one electron. The phenomena controlling the magnitude of $\overline{V}_e$ at high electron energies may thus be somewhat different from those at low electron energies. The same effect of course exists in the measurement of the excitation probability of single energy levels for electrons of similar energy.

The Change in Thermal Energy Which Accompanies a Change in Magnetization of Nickel

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(Received December 7, 1934)

A new method is described for measuring the very small changes in thermal energy which occur when the magnetization of a ferromagnetic substance is altered. The method is applied to an investigation of the phenomenon as it appears in a specimen of hard drawn nickel rod. As the nickel is carried through a half cycle of magnetization, commencing with maximum magnetization, the thermal energy decreases until (approximately) the knee of the hysteresis curve is reached. This is followed by a large increase as the steep part of the curve is traversed, and then by a much smaller increase as the half cycle is completed. The behavior of nickel is in contrast with that of carbon steel, for which Ellwood found an *increase* in thermal energy over the initial stage and a *decrease* over the final stage of this process.

INTRODUCTION

AN adiabatic alteration in the magnetization of a ferromagnetic substance is always accompanied by a change in temperature. Energy of some other form is converted into heat, or *vice versa*. When the substance is carried through a *complete* magnetic cycle the thermal energy increases by an amount which can be calculated from purely magnetic data. Experiment reveals, however, that in some materials this increase is the end result of a series of changes, alternately positive and negative, associated with consecutive portions of the cycle. The objects of the present paper are, first, to describe a new experimental method for investigating this phenomenon, and second, to describe the phenomenon itself as it appears in a specimen of hard drawn nickel rod.

The cognate investigation upon carbon steel has been reported in this Journal by Ellwood,[1] who measured the change in temperature accompanying change in magnetization of an array of 104 specimens. The present method differs from Ellwood's in that the energy change is measured directly, so that the specific heat does not intervene, and the number of specimens required is reduced to one.

In brief the method is as follows: The specimen, in the form of a right circular cylinder 1 mm in diameter and 35 cm long, is placed axially in a cylindrical calorimeter about which is wound a magnetizing solenoid. Thermocouples in thermal contact with the specimen permit changes in its temperature to be noted, and a means is provided for passing a known electric current for a known time interval through the length of the specimen. The change in thermal energy accompanying a given change in magnetization is then equal to I^2Rt, where R is the resistance of the specimen, and I and t are the current and time interval required to produce therein a temperature change equal in magnitude to that which accompanied the change in magnetization. From the energy change thus measured is subtracted the contribution arising from eddy currents. The remainder is the subject of the present investigation.

APPARATUS

(a) Material

The specimen material upon which observations are here reported is hard drawn nickel containing the following percentages of impurity: Cu, 0.07; Fe, 0.18; Mn, 0.044; Si, 0.21; C, 0.065. The specimens were prepared especially for this research by the International Nickel Company.

(b) The calorimeter and solenoid

The calorimeter and solenoid are those used by Ellwood, and are described in detail in the paper cited above. A large inductance is added to the solenoid circuit to reduce the eddy current effect as much as possible. The thermal environment of the specimen is the same as in Ellwood's method, except that the specimen is not imbedded in rice flour and the calorimeter is not evacuated.

[1] W. B. Ellwood, Phys. Rev. **36**, 1066 (1930).

(c) The thermocouple system

The thermocouple system is constructed as follows: Longitudinal grooves 1.5 mm wide and 1 mm deep are cut opposite each other along a hard rubber cylinder 3/16 inch in diameter and 8 inches long. Sixty turns each of copper and constantan ribbon are wound side by side on the cylinder in a shallow helical groove of 2 mm pitch. The direction of winding is reversed every 15 turns. The cross section of the copper ribbon is 1 mil by 15 mils, and of the constantan 2 mils by 20 mils. Along the centers of the two longitudinal grooves proximate turns of copper and constantan ribbon are soldered across with a minimum amount of soft solder. The copper ribbon is then clipped from one side of the hard rubber cylinder and the constantan from the other. The result is sixty pairs of thermocouples in series, in the form of a single continuous winding. Alternate junctions lie in two rows running down the centers of the opposite grooves. Over each row of junctions is placed a strip of phenolized paper 0.4 mil thick: upon one is laid the specimen rod and upon the other a similar rod of copper. The rods are pushed well down against the junctions and are held in place with a few turns of silk thread. Thermocouple leads are soldered to the terminal sections, current leads to the extremities of the specimen, and the assembly is mounted in the calorimeter.

The thermocouple leads are connected through an inductive loop and switch to an L and N galvanometer which has a critical damping resistance of 12 ohms, a period of 10 seconds, and a sensitivity of 103 mm per microvolt at a scale distance of 6 m. The current leads are connected through a variable resistance, battery, and milliammeter, to a timing switch. The over-all sensitivity of the specimen-thermocouple-galvanometer system is 629 ergs per cm cube per mm galvanometer deflection. Galvanometer deflections can be read to 0.2 mm.

(d) The timing switch

The timing switch is a two sector rotating contactor driven by a synchronous motor at a speed of one revolution in eight seconds. The contact interval, as measured on an oscillograph, is 1.02 seconds for one sector and 0.508 second for the other. An auxiliary switch in the circuit permits the use of either sector at will.

Method of Measurement

(1) Magnetic data descriptive of different magnetic cycles in the specimen are secured by the usual ballistic method. The resistance per unit length is measured with a Kelvin double-bridge. The thermocouples are then attached to the specimen and the assembly is mounted in the calorimeter. The temperature control system of the calorimeter is allowed to operate undisturbed until thermal equilibrium is established. The latter is indicated by a steady zero deflection of the galvanometer.

(2) The energy calibration curve of the assembly over the anticipated range of galvanometer deflections is obtained by varying the current which flows through the specimen when the timing switch is closed. The curve shown in Fig. 1 is typical. Observations made with the 1.02 second time interval are indicated by circles and those with the 0.508 second interval by dots. The maximum deflection of the galvanometer is observed in both these and the magneto-thermal measurements.

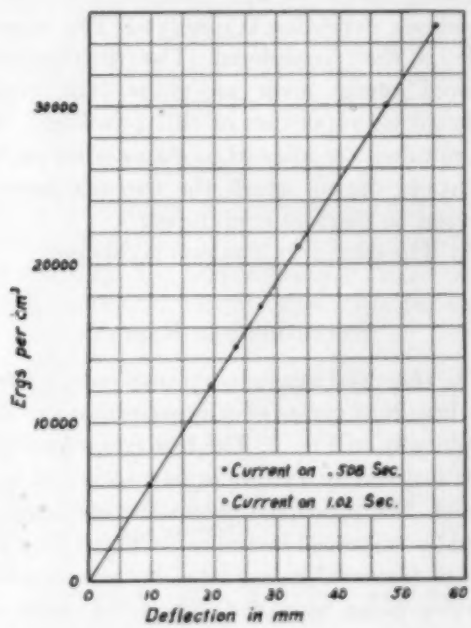

Fig. 1. The energy calibration curve of the thermocouple system.

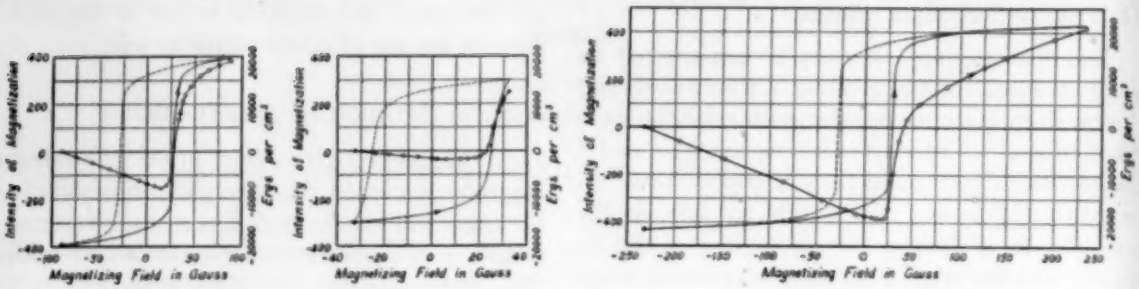

FIG. 2. The magnetic and thermal energy relations associated with different magnetic cycles in hard drawn nickel rod.

(3) The specimen is placed in the desired cyclic magnetic state by repeated reversals of the magnetic field, and left in the condition of maximum magnetization for the cycle. At the same time the inductive loop in the galvanometer circuit is so oriented that no net electromotive force is induced in the circuit when the magnetizing field is varied. The criterion for this adjustment is equality of the indicated magneto-thermal energy changes which accompany consecutive half cycles of magnetization. The adjustment does not depend upon the amplitude of the cycle.

(4) The magnetizing current is varied from its maximum to some lesser value by a single switching operation, and the accompanying galvanometer deflection is observed. The magnetic cycle is then completed. The distribution of thermal energy over an entire half cycle is obtained by repetition of this procedure. Some five minutes are allowed to elapse after each observation, during which the thermocouples are restored to thermal equilibrium.

(5) The energy calibration is checked.

EXPERIMENTAL RESULTS

The observed magneto-thermal energy changes for three half cycles of magnetization are shown graphically in Fig. 2. The hysteresis loop of the cycle is given by a curve in part solid and in part dotted. The solid part shows the magnetic path actually traversed in the experiment. The direction of traversal is indicated by arrows and the starting point by a dot. The solid curve upon which the observations are plotted gives the relation between total thermal energy and magnetic field intensity as the path is traversed. The data for the largest magnetic cycle are given in Table I.

TABLE I. *Energy change data for the largest magnetic cycle.*

H (gauss)	J (gauss)	Energy change (ergs/cm³)	H (gauss)	J (gauss)	Energy change (ergs/cm³)
−232.0	−427	0	23.1	−267	−18,600
−196.0	−423	− 2,890	24.4	−260	−17,100
−147.0	−413	− 6,720	29.5	138	− 9,750
− 85.4	−397	−11,450	35.9	310	− 2,960
− 44.0	−377	−15,100	44.0	345	1,640
− 19.7	−355	−17,300	57.5	368	4,900
− 7.7	−341	−18,200	86.3	393	8,540
0.0	−330	−18,600	125.0	406	12,700
7.7	−314	−18,900	148.0	413	14,700
13.7	−299	−19,100	199.0	424	18,700
19.7	−280	−19,300	232.0	427	21,200

The curves of Fig. 3 show what occurs when an attempt is made to retrace a magnetic path before the half cycle is completed. The dotted curve is that for the complete half cycle.

The foregoing observations must be corrected by a small amount representing the thermal energy associated with the eddy currents in the specimen. This correction will be calculated on the assumption that the magnetic field of the eddy currents is small in comparison with the impressed field, i.e., on the assumption that the penetration of the impressed field into the specimen is perfect.

Let W denote the thermal energy per cm cube associated with the eddy currents generated in a time t during which the induction in the specimen changes at the rate dB/dt. Then

$$W(\text{ergs}) = (r^2/8\times 10^9\rho)\int_0^t (dB/dt)^2 dt,$$

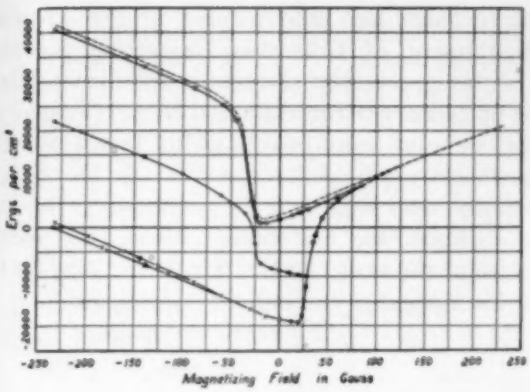

FIG. 3. The thermal energy changes which occur when an attempt is made to retrace a magnetic path before the half cycle is completed.

where r is the radius of the specimen rod in cm, and ρ the specific resistance of the specimen material in ohms per cm cube. But $dB/dt = (\partial B/\partial H)(dH/dt)$, and $H = H_1 + H_2(1 - \exp -[Rt/L])$, where H_1 is the initial and H_2 the final value of the magnetizing field, and R is the resistance and L the self-inductance of the solenoid circuit. Hence

$$W(\text{ergs}) = (r^2R/8\times 10^9\rho L)\int_{H^1}^{H_2}(\partial B/\partial H)^2(H_2 - H)dH.$$

The adequacy of this formula is established as follows: W is evaluated for a half cycle by numerical integration with values of $\partial B/\partial H$ obtained from the hysteresis loop of the specimen, and is subtracted from the observed total thermal energy change for the half cycle. The difference should exactly equal the energy measured by one-half the area of the hysteresis loop. The results for the three different half cycles are given in Table II, in which also is indicated the precision of the magnetic and thermal measurements.

TABLE II. *Energy values for the three different half cycles (ergs/cm³).*

—A—	—B—	—C—
13,000±300	12,600±200	12,500±200
19,200±400	19,200±200	19,000±200
20,400±400	21,200±200	20,500±200

A. Magneto-thermal energy, from the hysteresis loop.
B. Total energy by calorimetric measurement.
C. Magneto-thermal energy, by calorimetric measurement.

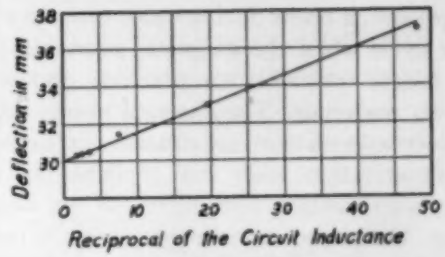

FIG. 4. The relation between the total thermal energy per half cycle and the reciprocal of the self-inductance of the magnetizing circuit. (1 mm def. = 629 ergs per cm³.)

Each point on the thermal energy curves can be corrected by performing the appropriate numerical integration. This has not been done in the present instance, since the correction is at most small.

A second over-all check on the magnetic and thermal measurements is obtained in the following way: The total thermal energy per half cycle of magnetization is observed as a function of the self-inductance, L, of the solenoid circuit, and the value corresponding to L infinite is obtained by extrapolation. This, again, should exactly equal the energy measured by one-half the area of the hysteresis loop of the specimen. A graph of the total energy as a function of $1/L$ is shown in Fig. 4. The observed linearity of the relation lends additional support to the formula for W, and the extrapolated value of the energy per half cycle agrees within the experimental error with those given in Table II.

DISCUSSION OF RESULTS

It is of interest to contrast the behavior of nickel with that of carbon steel as reported by Ellwood. Fig. 5 is a reproduction of one of Ellwood's curves. It will be noted that the energy

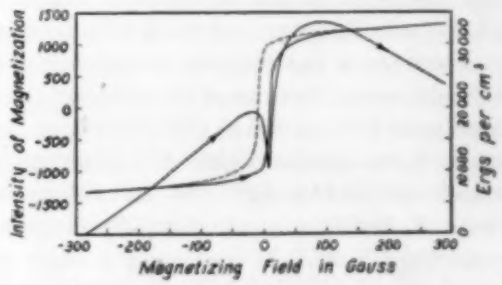

FIG. 5. Magnetic and thermal energy relations in carbon steel (after Ellwood).

changes which occur during those (end) portions of the cycle when the magnetic phenomena are most nearly reversible are precisely opposite in the two materials. The thermal energy of the steel increases on demagnetization and decreases on magnetization, while that of nickel decreases on demagnetization and increases on magnetization. The phenomenon is the subject of further research in this laboratory.

In conclusion the writer desires gratefully to acknowledge her indebtedness to the Physics Department of Columbia University for the facilities generously placed at her disposal; to the officers of the International Nickel Company, who were at considerable pains to secure the specimens used in the research; to Dr. S. L. Quimby, who suggested the problem; to Dr. W. B. Ellwood, for his counsel during the early stages of the work; and to Mr. C. F. Wiebusch, for his assistance throughout its progress.

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An Investigation of the Magneto-Optic Method of Chemical Analysis

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(Received December 21, 1934)

An apparatus similar to that used by Allison in his magneto-optic method of chemical analysis was set up in an effort to verify the existence of the sharp Allison minima. Many visual observations were made, but only occasionally did readings of possible minima occur in more than random groupings. Where these apparent minima did occur, it was thought that they could be explained as being due to such factors as sticky places on the trolley felt by the hand on the hand wheel control. When a motor control was used on a later apparatus, the distribution of readings of possible minima was no more than a chance distribution. Objective tests were made of the variation of intensity of light with trolley position by a photographic method. In this photographic method the effect of spark fluctuations was eliminated by comparing the intensity of the light passing through the cells with that of a comparison beam direct from the spark. Individual runs by this method showed no minima and were good to three percent. When several runs were averaged, the resultant intensity curve showed no variations greater than one percent. Eye tests showed that the writer could not have detected an intensity change visually of less than three percent on the magneto-optic apparatus. These results indicate that the minima occasionally seen by the writer on his apparatus have no objective reality. A broad minimum of the type described by Slack and by Webb and Morey was obtained by the photographic method for CS_2.

IN an effort to verify the existence of the sharp minima seen on the "magneto-optic apparatus" by F. Allison and others, an apparatus similar to that of Allison was set up in the physics department in September, 1933. The apparatus is shown schematically in Fig. 1. P is a 25,000 volt Thordarson type R transformer. G is a 4 mm spark gap between magnesium rods 4 mm in diameter. The size of the rods and the gap length were both varied at different times. L is a lens to form parallel light, F a filter to give monochromatic blue light. N_1 and N_2 are nicol prisms. B_1 and B_2 are cylindrical Pyrex cells, B_1 containing CS_2 and B_2 containing a water solution of some inorganic acid or salt. H_1 and H_2 are two similar helices, of from 20 to 90 turns (usually 50 turns) of No. 18 copper wire wound on Bakelite cylinders 3.5 cm in diameter and 14 cm long. T_1 and T_2 are trolleys to vary the relative lengths of the parallel wire paths to the coils. The trolleys are of No. 18 copper wire, the wires being spaced 20 cm apart. The length of the fixed trolley was varied from 2 to 7 meters. Sliding copper bars were used as contacts on the movable trolley. Values of the capacity C were varied from 0.0008 mf to 0.005 mf, both glass and mica condensers being used.

The Allison minima have been reported[1] to appear when a certain difference in wire path length to the two coils is obtained, these differ-

[1] F. Allison and E. J. Murphy, J. Am. Chem. Soc. **52**, 3796 (1930).

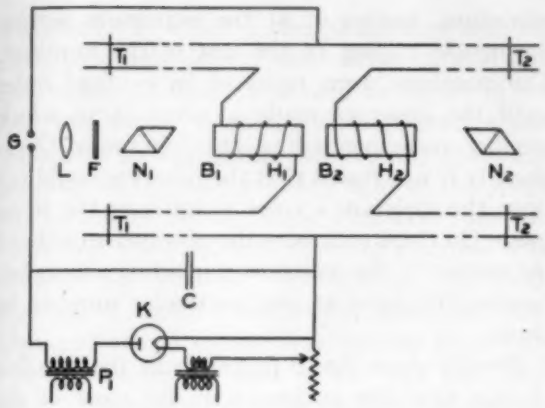

FIG. 1. Magneto-optic apparatus.

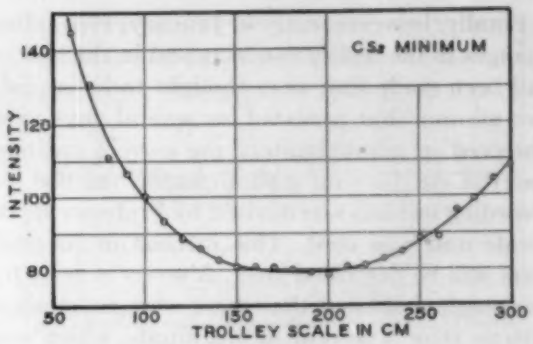

FIG. 2. Minimum with CS_2 in both cells, by photographic method.

ences being characteristic of the compounds in cell B_2. Since in practice one trolley is kept fixed, the minima appear at certain scale readings on the movable trolley.

These minima are reported to have been observed with several arrangements and variations of the above apparatus. The methods that have been tried by the author will be listed. The original method[1] is with "nicols crossed and coils opposed." That is, the two nicol prisms N_1 and N_2 have their planes of polarization perpendicular and the magnetic fields in the two helices are in opposite directions. In this method only light which experiences a net rotation in the two cells passes the second nicol prism. Another arrangement for viewing the minima[2,3] is with "nicols parallel and coils aiding," i.e., the planes of polarization of the two nicol prisms are parallel, and the currents in the two coils are such that the magnetic field goes in the same direction through each coil. In this case the effect of a rotation in either cell is to diminish the intensity of the light. A third nicol is used to cut down the intensity to the desired low value. With this method the minima have been reported with a variation of the apparatus in which the main spark current does not flow through the coils.[4] In this case the trolley system is connected across the spark gap through two small condensers.

Minima have been reported with a steady source of light, the spark still being used in connection with the electrical circuit, both with nicols crossed[1] and parallel.[5] They were seen when only one-half of the bilateral trolley system was used,[5,6] and have been reported with unrectified current to the spark.[6] Allison observed the minima with the trolley in motion. Latimer and Young used a static method in which the trolley was moved along in 2 mm steps, the observer looking at the spark only when the trolley was stationary.

In trying to locate the minima, the writer took repeated observations with a dilute solution of HCl in the cell B_2. The arrangement with "nicols crossed and coils aiding" was used. In each observation the observer would move the trolley by means of a hand wheel through the region in which minima were expected from published results, stopping whenever the light appeared less intense, and recording the position of the trolley. No assistant was needed, as the trolley position was read by the observer through a telescope which was directed on the scale by a system of mirrors. The results of a number of runs were then examined for coincidences in readings, and the positions of these were carefully examined. For several months no "minima" were seen that survived this scrutiny, though many combinations of the values of the various constants of the circuit were tried.

[2] F. Allison, J. H. Christensen and G. V. Waldo, Phys. Rev. **40**, 1052 (1932).
[3] E. R. Bishop, C. B. Dollins and I. G. Otto, J. Am. Chem. Soc. **55**, 4365 (1933).
[4] L. B. Snoddy, Phys. Rev. **44**, 691 (1933).
[5] G. M. Wissink, Physics **5**, 31 (1934).
[6] Fred Allison, J. Chem. Ed. **10**, 70 (1933).

Finally, however, early in January, 1934, after changes in the trolley contacts and in the helices had been made that were thought to be crucial, two minima that persisted for several days were observed in approximately the correct position for HCl. At this time a photographic method for recording minima was devised by Professor R. B. Brode and was used. This method in its final form will be described later. A series of tests by this method showed that there were no minima greater than 3 percent in magnitude, which was as far as the accuracy of the method was extended at that time. Further visual tests in the region showed that the minima seen were not persistent in respect to position of the trolley.

The broad minimum for the case of CS_2 in both cells was photographed and the curve for this is shown in Fig. 2. As can be seen, this minimum extends over several meters. This type of minima is adequately discussed by F. G. Slack[7] and by J. S. Webb and D. R. Morey.[8]

Then there followed a series of alternate visual and photographic tests for different solutions and varying spark conditions. In no case were possible visual minima confirmed by the photographic method, nor did they persist visually after negative results from the photographic method had been obtained.

Tests were made to determine how small a variation in intensity could be detected on the Allison apparatus, and with what optical arrangement this could be done. The intensity of the spark or of a steady mercury source was regulated to the usual value by two nicol prisms nearly crossed. A third nicol prism was mounted so that it could be rotated between two positions with respect to the second nicol, introducing an artificial minimum of any desired magnitude. Care was taken so that the observer could not see the assistant operating the nicol, nor could he see any movement or change except such as might appear in the intensity of the beam of light. In most of the tests the assistant called out a series of two or more numbers or letters. As one of these numbers was called, the assistant would turn the nicol to the position which gave the minimum, leaving it at the maximum setting during the calling of the rest of the numbers. The numbers were repeated in cyclical order until the observer made a guess as to which number corresponded to the minimum. Occasionally it was found that the observer could tell from the assistant's voice which was the minimum. On these occasions the observer would call the numbers, the assistant remaining silent, but turning the nicol at any particular number he chose.

Results show that 3 percent was the smallest change that the author, who did most of the observing for the Allison minima, could detect, and this with no reliability. Out of 62 trials at 3 percent taken in seven tests over a period of two months, he was right 42 times and wrong 20 times, the reliability varying from day to day. Usually anything over a $4\frac{1}{2}$ percent change could be detected with certainty, although on one day a 13 percent change was indistinguishable. Results were somewhat more consistent with a steady source than with a spark source, but the limit appeared to be the same. Tests of different types of comparison fields showed that, of those available, the best was a Lummer-Brodhun cube in which a central elliptical field was compared to an annular ring about it. The presence of the comparison field lent a greater degree of certainty as to the presence of the intensity change, especially for "inexperienced observers," but did not greatly extend the range of detectability. A change of 2.2 percent was the smallest change successfully "guessed at" by any observer under the conditions of the experiment. The use of extremely low intensities did not aid in observing these known changes.

It is interesting to note that when the control nicol prism was shifted between two positions "A" and "B" for which there was an intensity change too small to be easily distinguished, the light could be made to appear to change in intensity at each reversal of position, quite regardless of the actual direction in which the change was taking place. The only stimulus required for this apparent intensity change was the knowledge that the nicol was being shifted in position.

A visual trial was made of a variation of the apparatus reported to give minima recorded by a

[7] F. G. Slack, J. Frank. Inst. **218**, 445 (1934).
[8] J. S. Webb and D. R. Morey, Phys. Rev. **44**, 589 (1933).

photo-cell,[5] in which a steady mercury arc was used for a light source with nicols parallel and coils aiding. A spark was used as before in the electrical circuit. With this arrangement, it was impossible to distinguish visually any change in intensity of the blue mercury light as the spark was turned on. Nevertheless, a series of runs was made over the regions of expected minima, with readings of "minima" recorded in the usual manner. A toothed cardboard wheel of equal open and closed sectors was rotated by a synchronous motor so that it cut out the light passing through the cells for half a cycle. Just as great consistency was obtained in the readings of minima when the closed sectors cut out the light during the active half of the cycle as during the inactive half, the observer not knowing until after the run had been made whether the stroboscope was in or out of phase with the spark. In neither case were readings any more grouped than might be expected from a random distribution.

Using the spark as a source of light, coincidences in minimum settings were sometimes obtained that were unlikely to occur by chance. In one case when a possible minimum at a trolley scale reading of 148.7 cm was reported twice by a visitor to the laboratory, especial care was taken to avoid subjective influences. The writer acted as observer, operating the hand trolley, while W. H. Thurston watched the trolley scale and recorded the positions at which minima were called. The observer did not know the position of the trolley at any time during the run, and after announcing each minimum he moved the trolley about arbitrarily to try to lose any muscular sense of the exact position of that minimum. The fact that the observer thought that the trolley was progressing down the scale between each recorded position shows that this attempt was successful. The positions of the reported minima were:

150.6 150.7 150.7 150.0 (weak) 148.7

At the time this was regarded as fairly convincing evidence of a minimum at 150.7 and possibly one at 148.7, with three coincident readings of each out of seven tries. Failure to confirm either as a true minimum led us however

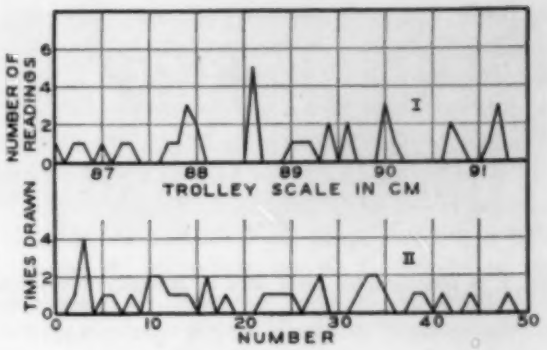

FIG. 3. Curve I gives the number of readings of minima recorded by the author at different positions of the trolley in the region in which the $CaCl_2$ minima were expected. Curve II is a random curve for comparison, obtained by drawing numbers.

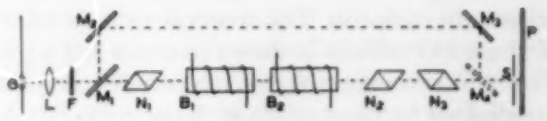

FIG. 4. Optical arrangement used in the photographic method.

to explain them as "sticky" places on the trolley wires, which, felt unconsciously by the hand through the control wheel, gave sufficient stimulus to cause one to "see" the looked-for effect. Another subjective trouble that was noticed occurred when the observer tried to set accurately on a minimum. Whenever a prospective minimum was located by a progressive motion along the trolley, he would try to set on it by rolling the trolley slowly back and forth through the approximate position. At the center of each swing a "subjective minimum" was automatically seen, unless carefully guarded against.

Partly on account of these two difficulties a new trolley system was set up in which the trolley was moved by an electric motor. Other changes were made in the apparatus in the new arrangement, such as in the form and length of the trolley wires, in order to try to avoid any unknown fundamental defects in the particular apparatus. With the new arrangement, a dilute solution of HCl and $CaCl_2$ was examined for possible minima in the expected regions, using the apparatus with the nicols parallel and coils aiding.

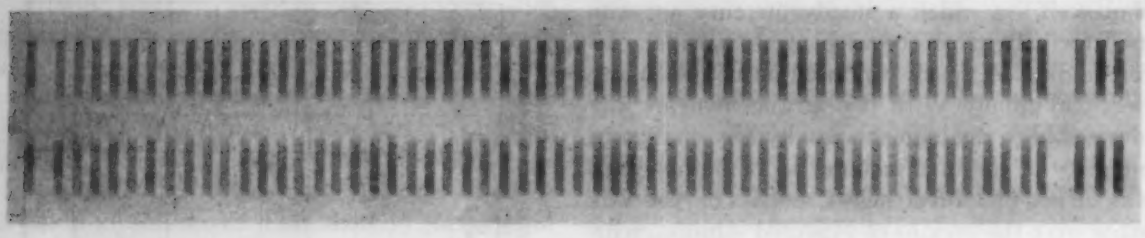

FIG. 5. A photographic plate used in intensity measurements. Microphotometer measurements of this plate gave the intensity curve II, Fig. 6.

Readings were taken over the 5 cm trolley interval in which the $CaCl_2$ minima were to be expected. In the course of 15 runs over this interval a total of 36 minima including repetitions were observed, there being 1 to 4 observed minima in each run. The frequency distribution of these 36 readings is shown in curve I, Fig. 3. That this is comparable to a chance distribution is indicated by comparison with curve II, Fig. 3. This second curve was obtained by placing in a box 50 numbers corresponding to the 50 possible settings on the 5 cm trolley interval. Thirty-six numbers were then drawn from the box 1 to 4 at a time to correspond to the 36 minima recorded in groups of 1 to 4 found in each actual run through the region. The numbers were replaced after each drawing. Curve II is the frequency distribution of the numbers drawn.

A final series of photographic tests was made over this and other regions of the trolley. These tests were based on the static method of observation used by Latimer and Young. The light passing through a 1 mm slit S (Fig. 4) fell on a $1\frac{1}{2}$ by 6 inches Eastman 33 photographic plate. The upper half of the slit was illuminated by light passing directly through the cells B_1 and B_2. The lower half of the slit was illuminated by a comparison beam that did not pass through the cells. This comparison beam was reflected from the main beam to a side path by the plane glass plate M_1 and the mirror M_2, and was reflected back into the original line of direction by the mirrors M_3 and M_4. An exposure of 20 seconds was made in one position of trolley and plate. The plate was then moved 2 mm, the trolley moved 1 mm, and another exposure taken. Thus two series of shadow images of the slit were formed on the plate (Fig. 5), one depending on the light intensity coming through the cells and the other showing the relative intensity of the spark during this time. On each plate there were several exposures taken with a piece of plane glass in the main beam, introducing an artificial 9 percent minimum for calibration purposes. Each series of images was then microphotometered, and the throw of the microphotometer measured for each image. The ratio of the throw for any image formed by the main beam to the throw for the corresponding image of the comparison beam gives a measure of the light coming

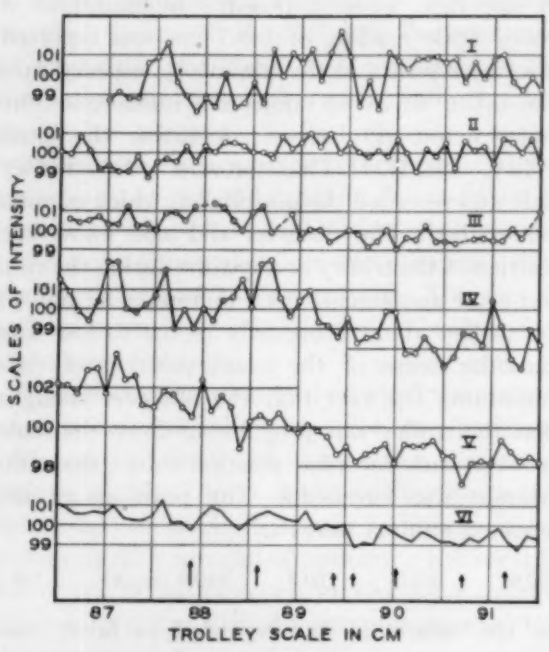

FIG. 6. Curves I to V are intensity curves from individual photographic plates. Curve VI is the average of these. The arrows indicate positions of possible visual minima. There is no apparent consistency between the visual minima and the intensity curves.

through the cells that is independent of spark fluctuations. By a suitable factor determined for the plate from the 9 percent calibration minima, this ratio was converted into percent variation of the light intensity. The spark was adjusted to a more steady state before each run by varying the resistance in series with the filament of the kenetron so that a definite number of condenser discharges per cycle (usually 2) took place, as determined by the number of sparks seen in a revolving mirror driven by a synchronous motor.

Curves I, II, III, IV and V, Fig. 6 are individual runs over the same 5 cm region in which $CaCl_2$ minima were expected. Curve VI is the average of these. As can be seen, there is no correspondence in minima of more than a random nature between any of the curves of Fig. 6. The arrows in Fig. 6 represent visual minima observed in 15 runs over the same region. The length of each arrow represents the frequency of observation of the minimum. These are the same minima shown in Fig. 3. Since the accuracy of locating minima visually was 3 percent at best, and since the photographic method is good to 2 or 3 percent on individual runs and good to about 1 percent when several runs are averaged, it is clear that this objective test does not reveal the existence of any real minima on the apparatus used. The author believes, as a result of these tests, that such minima as he saw from time to time can be explained as due to physiological or psychological factors.

As the final photographic tests described were being made and after all visual work had been completed, an article by F. G. Slack[7] in the *Journal of the Franklin Institute* appeared. This article contains a very complete bibliography of the subject. It is interesting to note that although these two investigations were carried out completely independently and initially with different viewpoints, the observations made and the conclusions drawn from them by the observers are in essential agreement.

In conclusion, the author wishes to express his appreciation to Professor R. B. Brode, who proposed this study and directed the first part of the work, to W. H. Thurston and R. Leonard for their aid in assembling the apparatus and in observing, to Professor L. B. Loeb for his help in preparing this report, and to many other members of the physics department for their interest and suggestions.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveres in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twentieth of the preceding month; for the second issue, the fifth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

X-Ray Wavelength Scales

(1) In a recent paper the author[1] presented a new method for obtaining x-ray terms and discussed the experiments of Kretschmar and of Robinson, Andrews and Irons, on the energies of photoelectrons ejected by x-rays, in the hope of deciding between the crystal and ruled grating wavelength scales. The discussion was based on current values of the universal constants and the result was this: Measured energies of photoelectrons are 0.36 percent higher than those computed from crystal values of x-ray wavelengths, which in turn are 0.25 percent higher than values deduced from grating measurements. Thus the photoelectric measurements appeared to support the validity of the crystal scale, but it was specifically stated that errors in the values of universal constants might be large enough to reverse such a conclusion.

New experiments by Bearden and Shaw[2] show that refractive index measurements yield wavelengths in agreement with unruled grating values, and Bäcklin[3] finds that the ruled grating wavelength of Al $K\alpha$ exceeds the crystal value by the *same percentage discrepancy* which Beardon has consistently found for lines of much shorter wavelength. These experiments indicate very strongly that ruled grating wavelengths are essentially correct and that crystal wavelengths differ from them by a constant factor because of the use of an incorrect value of the calcite spacing, d. This spacing is connected with the electronic charge e by the equation

$$d = fe^{1/3}, \tag{1}$$

where f is a factor containing quantities which are accurately known. It will conduce to clarity if we remind the reader that there are really three scales to be considered, based on three methods of obtaining d, as follows:

(I) The so-called crystal scale; $d_c = 3027.85 \cdot 10^{-11}$ cm at 18°C. This value is obtained by using $e = 4.7668 \cdot 10^{-11}$ e.s.u.

(II) Conventional scale of Siegbahn. Wavelengths are expressed in X. U., and by definition the calcite spacing d_s is 3029.45 X. U.

(III) The grating scale. Using Bragg's law and grating wavelengths, one obtains a value d_g for the calcite spacing. Eq. (1) then gives the corresponding value of e.

Using the third method, Bäcklin gets

$$e = 4.805 \cdot 10^{-10} \text{ e.s.u. (Precision not stated.)}$$

in agreement with Bearden's[4] value $(4.806 \pm 0.003)\ 10^{-10}$ e.s.u.

(2) Adoption of d_g removes, of course, the discrepancy between grating and crystal wavelengths. The purpose of this note is to show that *if we adopt the Bearden-Bäcklin value of e and the Shane-Spedding*[5] *value,* $e/m = (1.7579 \pm 0.0003)\ 10^7$ e.m.u./g., *then the puzzling discrepancy between measured photoelectron energies and those computed from x-ray wavelengths is entirely explained.*

The argument depends on the fact that

$$e^{5/3}/h = (R_\infty c^2/2\pi^2)^{1/3}(e/m)^{1/3}. \tag{2}$$

The factors in the first parentheses are accurately known, and $e^{5/3}/h$ is relatively insensitive to errors in e/m, so we know its value very well indeed. The consequence is, that in the writer's above-mentioned paper we should decrease e/m by 0.07 percent, and e/h by 0.56 percent, which means that ν/R values of photoelectrons are decreased by approximately 0.63 percent.

After my paper had gone to press, Professor Robinson applied an average correction of -0.15 percent to his photoelectron energies, because of a recalibration of his apparatus. This means that the discrepancy between the Robinson-Kretschmar photoelectron energies and those obtained from ruled grating wavelengths should have been given as 0.54 percent. Finally, use of the new values of e and e/m brings the photoelectron energies to a position 0.09 percent below ruled grating values. The probable errors of the experiments involved are quite sufficient to account for this small residual; indeed, its sign is what one would expect as a result of retardation of photoelectrons in the films from which they are ejected and work function of the films (a suggestion which I owe to Professor Paul Kirkpatrick).

(3) Ruark and Maxfield[6] have computed a new set of term values for the radioactive elements and have applied them to problems of beta- and gamma-ray spectra. These terms, expressed in international electron volts, must all be reduced by 0.27 percent if we employ the new values of e and e/m. However, *voltage* values for secondary beta-rays (roughly proportional to e/m) are reduced by only 0.07 percent. The data in Table II should be recomputed, but so far as I can see all the physical results of the paper are unaltered.

(4) On the basis of the new values of e and e/m, the reciprocal of the fine-structure constant assumes the value 137.04; I shall not attempt to discuss its probable error.

ARTHUR EDWARD RUARK

Department of Physics,
University of North Carolina,
January 20, 1935.

[1] Ruark, Phys. Rev. **45**, 827 (1934).
[2] Bearden and Shaw, Phys. Rev. **46**, 759 (1934).
[3] Bäcklin, Nature **135**, 32 (1935).
[4] Bearden, Phys. Rev. **37**, 1210 (1931).
[5] Shane and Spedding, Phys. Rev. **47**, 33 (1935).
[6] Ruark and Maxfield, Phys. Rev. **47**, 107 (1935).

Photography of Minima in Magneto-Optic Apparatus

Recently there has been developed in this laboratory a photographic method for the study of the minima of light intensity in the magneto-optic method of analysis observed visually by Allison and others. In view of the criticism this method has withstood and the failure of some investigators to operate the apparatus successfully, a letter communicating some positive objective tests of this nature seems to be in order at this time.

The magneto-optic apparatus is identical with that Allison[1] uses for visual work except that a Wollaston prism has been substituted for the analyzing nicol prism. The Wollaston prism is so placed that its two beams lie in a horizontal plane. The polarizing nicol is rotated until the two beams from the Wollaston are of approximately equal intensity. The two images of a narrow vertical slit placed just ahead of the Wollaston are brought to a sharp focus on a photographic plate by a single lens. Each picture is composed of two sharp lines, one being due to light polarized in a vertical plane and the other to light polarized in a horizontal plane. Any rotation in the plane of polarization of the light as it passes through the liquids in the apparatus will cause a brightening of one of the beams and an equivalent dimming in the other. The lines of each picture were examined with a conventional type microphotometer by using a vacuum thermocouple and a short period galvanometer. The line densities were read directly from the galvanometer deflection. The photographic plate, an Eastman Hyperpress plate, was racked by steps along a horizontal track so that 14 to 20 pictures could be made on a strip. The average plate contained several such strips. A synchronous motor operating an electrical switch made the time of exposure and the time between exposures uniform for all the pictures.

The pictures were made with the trolley alternately on the position of the minimum and off this position a centimeter or two. The positions of minima used were those found from repeated visual work. Clamps on the trolley wheel made these two positions constant for any series of pictures. Pure water blanks were first used for each compound studied and the pictures taken with the trolley on and off the position of a minimum characteristic of the compound to be introduced. To overcome any possibility of any mechanical characteristic of the apparatus or electrical circuit duplicate exposures were made for each picture with the current in the coils reversed to its original direction.

Table I represents the averaged results of 225 pictures of water run as blanks for 338 pictures of compounds. These pictures were made on a number of different photographic plates taken over a period of two months. The camera and its optical system were completely dismantled after each plate. The compounds examined included two inorganic acids and three salts all at a concentration of one part in 10^6 parts of water.

TABLE I.

Fields	Current	Compounds	No. of pictures	Algebraic ave. for water	Arithmetical ave. for water	No. of pictures
Assisting	Regular	+10.8	137	+0.45	1.9	89
Assisting	Reversed	−9.95	103	−1.44	1.44	54
Opposing	Regular	−8.0	30	−0.82	2.5	46
Opposing	Reversed	+9.1	68	−0.11	2.7	36

The values given in the above table are the percentages by which the difference in density of the two lines photographed when the trolley was on the minimum position differs from the corresponding difference in density when the trolley was at an off position. This is not the absolute intensity change seen when the trolley moves through a minimum.

It was found that for compounds in every case whether the fields were opposing or assisting a change in the direction of the current gave a corresponding change in the sign of the percentage. The water however varied with no regularity in sign. Both the algebraic and arithmetic averages are given for the water to show the random distribution of sign. The above table does not include the results of 200 pictures taken before an automatic timing device was used. They are, however, perfectly in accord with those listed.

These perfectly objective tests demonstrate the reality and the reproducibility of the minima. The minima are sharp since the on and off positions of the trolley differed by only a centimeter or two. They are characteristic of the compound since pure water blanks give much lower values than the same water and tube give after a trace of the compound has been added.

The work is being continued with a view of presenting a more extended paper.

GORDON HUGHES
ROY GOSLIN

Department of Physics,
Alabama Polytechnic Institute,
January 19, 1935.

[1] Allison and Murphy, J. Am. Chem. Soc. **52**, 3796 (1930).

Hyperfine Structure of the Cadmium Resonance Line

I have recently been experimenting with a liquid-air cooled Schüler tube, the cathode of which is a thin glass projection coated internally with cadmium. As a fairly rigorous test of the cooling, I have photographed by means of a Lummer plate the hyperfine structure of the resonance line at λ2288 $^1S_0-{}^1P_1$, which was observed by Professor R. W. Wood[1] to have a doublet structure of 0.38 cm^{-1}. With currents of 35 m.a. in my tube the line shows as a reversal with a separation of about 0.2 cm^{-1}, but with a current of 15 m.a., the separation is only about 0.08 cm^{-1}. Whether this is still due to a reversal or not, it is impossible to say. In any case, it gives an upper limit to the splitting of the $^1P_1$ term. The spark resonance line at λ2265 $^2S_{\frac{1}{2}}-{}^2P_{1\frac{1}{2}}$ appears to have a close hazy satellite on the short wavelength side.

A. G. SHENSTONE

Princeton University,
January 22, 1935.

[1] Wood, Phil. Mag. **2**, 611 (1926).

The Disintegration of Beryllium by Photons and Its Possible Bearing on the Mass of Be^9

Szilard and Chalmers[1] found that when beryllium was bombarded with the gamma-rays of radium in equilibrium with its decay products, neutrons were liberated, and could be detected by means of the radioactivity they excited in iodine. Meitner[2] showed that these neutrons excited radioactivity in I, Au and Ag, but not in Na, Si and Al. The former reactions involve the capture of a neutron, which, as Fermi[3] has shown, is most probable when the neutrons have little energy; while the latter three reactions involve the emission of an alpha-particle or proton, and probably have a higher probability when the bombarding neutrons have greater energies. Brasch and others,[4] working with x-rays, have obtained this disintegration at voltages between 1.5 and 2 mev.

In the present experiment, beryllium was bombarded with the x-rays from the tube in the Kellogg Radiation Laboratory. The tube is self-rectifying, and was supplied with 50 cycle a.c. at 0.9 mev peak. The electron current to the target was 2 m.a. The beryllium was located directly behind the tungsten target, in a bomb which was lowered inside the electrode. The ethyl iodide used as a detector for the neutrons was also in the bomb, just above the beryllium and in a Dewar vessel to prevent the heat generated at the target from reaching the ethyl iodide in the course of the irradiation, which lasted 40 minutes. The active iodine was separated from the ethyl iodide by the method of Szilard and Chalmers.[5] 200 g of beryllium and 375 cc of ethyl iodide were employed; the inside diameter of the bomb was 6.2 cm, and its overall length 25 cm. The intensity of radiation at 1 cm behind the target is calculated to be 2.5×10^4 r/min., on the basis of the measured intensity at 50 cm from the target and the known filtration in both cases.

The samples of iodine separated after irradiation were tested for activity with a quartz-fiber electroscope loaned by Professor C. C. Lauritsen. There was no increase over the background on the introduction of a sample. To check the sensitivity of the method, a test run was made with 370 mg of radium placed under the bomb in the position occupied by the target of the x-ray tube in the first experiment. The activation of the iodine in this case was easily measurable, initially more than doubling the cosmic-ray background. This poor yield in the case of the radium is to be attributed to the unfavorable geometrical conditions of necessity offered by the bomb; a much larger effect can be obtained by increasing the solid angles of irradiation.

Taking into consideration the relative intensities of the two sources of radiation, it may be said that an activation produced by the x-rays of one-one-thousandth the magnitude of that produced by the gamma-rays of radium would have been detected in this experiment. This may perhaps be reconciled with the statement of Gentner[6] that 0.9 mev radiation is most effective in the disintegration of beryllium, if one presumes that the efficiency of the process falls off sharply on the low-energy side of 0.9 mev, for the number of 0.9 mev quanta in the radiation produced in an x-ray tube excited with a.c. at 0.9 mev peak is very small.

If one is to suppose that beryllium is disintegrated into two alpha-particles and a neutron by a high energy photon, and that the enormously reduced yield just below a million volts found in this experiment indicates the existence of a genuine threshold for the phenomenon, then it seems possible that the mass of Be^9 is too high. If we fix the threshold at 0.9 mev and take the mass of the neutron as 1.0080, then, on our assumptions, the mass of Be^9 must be 9.0114, a result which explains the anomaly of the stability of Be^9, as well as Bonner and Brubaker's[7] results on the energy of the neutrons from Be bombarded with deutons. Miss Meitner's[8] result that radioactive B^9 is formed in the reaction

$$_3Li^6+{}_2He^4\rightarrow{}_5B^9+{}_0n^1\rightarrow{}_4Be^9+{}_1e^++{}_0n^1$$

is additional evidence for this mass of Be^9, as Professor Lauritsen has pointed out to us.

We are indebted to Professor Lauritsen for the electroscope, to Dr. Clyde Emery and the Cedars of Lebanon hospital for the radium source, and to the Seeley W. Mudd Fund for the support of this work.

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W. K. Kellogg Radiation Laboratory
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Pasadena, California,
February 2, 1935.

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Evidence for a Positron-Negatron Component of the Primary Cosmic Radiation

Recent studies of the cosmic-ray shower intensities and their dependence on latitude, elevation and direction have brought forth some new results which seem to throw important light on the nature of the primary radiation. For measuring the intensity of showers, three coincidence counters were mounted with their axes horizontal and at the vertices of an upright equilateral triangle. Immediately above the upper counter was a lead plate 1.2 cm thick and slightly larger than the cross-sectional area of a single counter. The counts thus recorded were corrected for accidental coincidences and the result was taken as a measure of the intensity of the shower producing radiation (I_s). The same three counters were also mounted in vertical line and the counting rate in this position, corrected for accidental coincidences and sidewise showers, was taken as a measure of the total radiation incident from the

TABLE I. *Shower and vertical intensities.*

Station	Geomagnetic latitude	Elevation (meters)	I_s Shower intensity (counts per min.)	$I_\perp$ Vertical intensity (counts per min.)	$I_s/I_\perp$
Swarthmore	50°	100	2.2	12.9	0.17
Vera Cruz	28°	20	2.3	11.9	0.19
Mt. Evans	50°	4300	15.0	36.8	0.41
Nevado de Toluca	29°	4300	11.4	28.2	0.40
Copilco	29°	2280	7.4	22.8	0.32
Parral	36°	1730	4.6	17.5	0.26

vertical direction ($I_\perp$). The ratio ($I_s/I_\perp$) of shower intensities to vertical intensities was thus independent of changes of sensitivity which might be feared in moving the apparatus from one station to another. The corrected rates and their ratios for six stations are given in Table I and they display the following interesting features. In the first place, the ratio ($I_s/I_\perp$) increases with elevation, showing that the showers are relatively more intense at high elevations. This agrees with the results of similar measurements[1] made in August, 1933, in Peru, and with the results of Rossi[2] in Erythrea. The second feature of interest is the fact that at high elevations $I_s/I_\perp$ does not vary with latitude, and at sea level it decreases with increasing latitude. Thus the high elevation showers are due to primaries which are affected by latitude to about the same extent as the total vertical radiation, whereas the sea-level showers are due to rays of such energies that they are not affected by these changes in latitude to as great an extent as $I_\perp$.

A second series of experiments was carried out on Nevado de Toluca in Mexico in which a similar shower measuring arrangement was used for investigating the azimuthal symmetry of the shower producing radiation. To obtain better directional resolution the counters, in this instance, were placed at the vertices of an isosceles triangle, 23 cm in altitude and 9 cm base, with the same plate of lead over the upper counter and parallel to the base. In two runs this arrangement was inclined from the vertical 35° and 49°, respectively, and at regular intervals it was rotated about a vertical axis between the east and west azimuths. The results of these experiments are contained in Table II and they show that the shower producing

TABLE II. *Shower asymmetry on Nevado de Toluca. Elevation 4300 m, geo. mag. lat. 29°.*

Zenith angle	$(I_w+I_e)/2$ (counts per min.)	$2(I_w-I_e)/(I_w+I_e)$
35°	3.70	$0.012 \pm .011$
49°	2.50	$0.018 \pm .010$
35° (without lead)	1.08	

radiation is almost completely symmetric about the meridian plane. For comparison it is noted that the total western radiation, measured with three counters in line, at the same station was 10 and 13 percent more intense than the eastern radiation at these same angles. It seems impossible to account for this symmetry by the failure of the apparatus to resolve directional effects since the shower intensities did show marked variation with the zenith angle. Also it was found by removing the lead that more than two-thirds of the counts recorded were due to showers produced in the lead and this presented a much larger area towards the azimuth in which it was pointing than to the opposite azimuth. Since shower intensities vary with latitude, they must be due to primary charged rays, and the azimuthal symmetry must mean that these are about equally divided between positives and negatives.

This suggests that the primary shower producing component consists of positrons and negatrons, while the radiation which produces the asymmetry measured by counters in line is due to more penetrating corpuscles, presumably protons. This is somewhat similar to the hypothesis proposed on other grounds by Compton and Bethe,[3] and is in line with the findings of Anderson, Blackett and others that the intermediate shower producing radiation probably consists of photons, for it is perhaps less difficult to account for the production of these photons by primary electrons than by protons. It is possible that some of the events which are recorded by the shower measuring arrangement can be produced by protons, and if so, these would represent a larger fraction of the total at sea level. This would seem to be the explanation of the asymmetry in showers found at sea level on the equator,[1] and of the slight asymmetry shown by the present measurements at high elevations in Mexico.

On the basis of the openings of the cones for rays of various energies, given in 1933 by Vallarta, the positive component alone seemed sufficient to account for the whole of the latitude effect.[1] The recent calculations of Lemaitre, Vallarta and Bouckaert,[4] on the other hand, give values for the openings of the cones such that the asymmetries and latitude effects can be made to accord with one another only by assuming the existence of a negative component as well. Estimates of the magnitude of this component will be made in a later publication.

These studies have been made with the support of the Carnegie Institute of Washington to which acknowledgment is made. I wish also to express gratitude to Mr. Lewis Fussell, Jr., for his help with the measurements and the reduction of data.

THOMAS H. JOHNSON

Bartol Research Foundation
of the Franklin Institute,
January 29, 1935.

[1] T. H. Johnson, Phys. Rev. **45**, 569 (1934).
[2] B. Rossi, Ricerca Scientifica **5**, 594 (1934).
[3] A. H. Compton and H. A. Bethe, Nature **134**, 734 (1934).
[4] I am indebted to the authors of this paper for sending me the manuscript in advance of publication.

The Value of the Electronic Charge

A notable contribution to our knowledge of the value of the electronic charge e has just been made by Schopper.[1] A method based on the original work of Rutherford and Geiger[2] and of Regener[3] was used, namely a simultaneous measurement of the number of α-particles emitted by a radioactive substance in a given time interval, and of the total charge carried by these particles. The final equation for e contains four factors, (1) a geometrical factor R, which measures the ratio of the number of α-particles counted to the number collected on the electrometer, (2) the average charge J, in int. coulombs, acquired per unit time by the electrometer, (3) the average number of α-particles $\bar{n}$ entering the counting chamber per unit time, and (4) the average multiple ϵ of the electronic charge carried per α-particle. In terms of these factors we have

$$e=(J\cdot R)/(\bar{n}\cdot\epsilon).$$

It is not possible, from the published information, to check the value or the accuracy of J and of R. We therefore confine our remarks to ϵ and $\bar{n}$.

The value of ϵ is slightly less than two, due to the repeated gain and loss of electrons by an α-particle, during its passage through matter. Schopper quotes values of 1.997 (Rutherford), 1.996 (Kapitza) and 1.992 (Henderson), and uses 1.995 ± 0.0015 as an average. We are unable to check any of these values. The data of Rutherford and of Henderson are shown most clearly in Fig. 3, p. 163 of Henderson's paper.[4] The ordinate y is the cube root of the relative abundance of doubly and singly charged α-particles from Ra C′, slowed down by foils of various thicknesses and materials. The abscissa is V/V_0, where V_0 is the initial velocity (1.922×10^9 cm/sec.) of the particles. All but one of the 25 experimental points shown in this figure lie quite accurately on the straight line $y=-0.830+6.466x$. For polonium α-particles, used by Schopper, the velocity corresponds to $x=0.827$. Hence $y=4.517$, $y^3=92.16$ and $\epsilon=(2\times92.16+1\times1)/93.16=1.989_3$. The mean error 1.5×10^{-3}, adopted by Schopper, is a very conservative estimate of the mean error of this new value.

Kapitza appears to have made no measurements in the desired velocity range. Hence 1.989_2 is the best average value. Schopper's results may be due to the erroneous assumption $x=1$, since the equation just quoted then yields $\epsilon=1.994_4$. Our new value of ϵ is 0.29 percent less than his adopted average value, and the resulting value of e is accordingly increased by the same amount. Using Schopper's own published values of R, J, $\bar{n}$ and ϵ, we find $e=4.766_{47}\times10^{-10}$ abs-*es*-units (he gives 4.768), whereas our new value of ϵ gives $e=4.780_1$.

To obtain $\bar{n}$, the average of many observations (n_0) of the number of α-particles per unit time, Schopper uses the formula $\Sigma y/\Sigma x$, where y is the counted number of particles reduced to a standard epoch (his N_0), and x is the corresponding time interval which varies from 9 to 23 hours.[5] This formula may be written $\Sigma x(y/x)/\Sigma x$, and obviously corresponds to weighting each determination of a slope y/x(=his n_0) proportional to the x interval. When the variations in n_0 are due solely to statistical fluctuations, this is the correct formula to use in order to give the most reliable average result $\bar{n}$. However, in calculating the mean error in $\bar{n}$, Schopper uses a formula applying only to the *unweighted* average $\Sigma(y/x)/k$, where k=number of observations. Since only about one-quarter of the individual n_0 values are given, we cannot check his result $\bar{n}=33.132\pm0.030$ counts per minute, but the value of $\bar{n}$, calculated from the published portion of the data, is $33.133_6\pm0.236$ percent, or ±0.244 percent when calculated by Schopper's formula. It is thus evident that the method of calculating the mean error makes a negligible difference.

Schopper justifies his assumption that the variations in n_0 are purely statistical, by showing that the observed proportional mean error in $\bar{n}$ agrees with the calculated value (the reciprocal of the square root of the total number of counted particles). The observed and calculated errors agree well, even in the case of the small portion of the data published, for which one finds the predicted error to be 0.19 percent, only slightly less than the observed values just given. Hence his adopted mean errors in ϵ and $\bar{n}$ appear reasonable, but whether the final probable error in e is as small as his adopted 0.1 percent seems more questionable, although we are not in a position to judge.

Our recalculated value 4.780 is 0.25 percent above the oil-drop value[6] (4.768 ± 0.005), but it is still far below the value 4.805 given indirectly by the grating wavelengths of x-ray lines, using the present accepted structure and constants of calcite. This last value of e results from the assumption that ruled grating wavelengths are 0.22 percent larger than Siegbahn's crystal wavelengths. This figure was obtained by Bearden[7] for wavelengths between 1.4 and 2.3A, and has just been accurately verified by Bäcklin,[8] for a wavelength 8.3A. It thus seems established that the discrepancy between the grating and crystal wavelengths is close to 0.22 percent, *independent* of wavelength, but the cause of the discrepancy remains as mysterious as ever.

RAYMOND T. BIRGE
EDWIN MCMILLAN

University of California,
January 25, 1935.

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[6] R. T. Birge, Rev. Mod. Phys. **1**, 1 (1929) and Phys. Rev. **40**, 228 (1932).
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Artificial Radioactivity Induced by Cosmic Rays

In these columns, J. E. I. Cairns[1] has recently presented experimental data on the frequency of "Stösse," which lead him to suggest that cosmic rays produce artificial radioactivity in the lead shields of his apparatus. His data are from two runs of 1344 and 1524 hours, respectively. In the first, he obtained 927 bursts, with 14 doubles, i.e., pairs of bursts separated in time by one minute or less. He states that this number of doubles is 94 times that to be expected from probability considerations. In the second

run, the results were 634 bursts and 5 doubles, or 164 times the probable number. No formula is given for computing the probable number, but it is easily derived. Suppose that N bullets, each one unit wide, are shot at a rapidly revolving disk, whose circumference is m units long; how many will hit a bullet which is already stuck to the target? The number of hits on the nth shot is $2(n-1)/m$, and therefore the total number of hits equals

$$\sum_{n=1}^{N} 2(n-1)/m = N(N-1)/m \doteqdot N^2/m.$$

Changing from a length scale to a time scale, and using minutes as units, we find that Cairns should have obtained 10.6 doubles in his first experiment, and 4.4 in his second. These deductions were tested experimentally by dealing 927 six-card hands from a large deck. The six-digit numbers so obtained were examined for pairs with a separation (Δ) of 50 or less. A Δ of 12.4 would correspond to a separation of one minute in Cairns' experiment. 5 pairs with $\Delta < 12.4$ were found. From the formula, it is seen that there should be as many pairs with a Δ between 0 and 12.4 as between n and $n+12.4$, if n is not too large. Averaging the number of pairs in the first four intervals of 12.4 units, we obtained 9.5 coincidences; the formula predicts 10.6. Therefore it is concluded that the laws of probability can account for the observed number of pairs of bursts, and therefore the artificial radioactivity hypothesis is unnecessary.

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January 25, 1935.

[1] J. E. I. Cairns, Phys. Rev. **47**, 194 (1935).

The Validity of the Applications of Electrodynamics

It is generally conceded that the theory of electrodynamics is formulated at present in an unsatisfactory manner. The most obvious difficulty is connected with the limitation of the applications to the point electron. This difficulty is not the most perturbing which we encounter, because we know its origin and could presumably avoid it if we could formulate a satisfactory theory of the structure of the electron.

The origin of the second difficulty—the one we wish to discuss—is hard to state specifically. The facts are that the properties of high energy particles and radiation as calculated from the existing theory do not agree very well with the experimental results. The calculations are very complicated, however; this complication makes it difficult to decide just what aspect of the theory needs revision. In this note we shall point out some features of the radiation theory whose formulation depends on the internal degrees of freedom of the electron. We shall show that the terms depending on these inner degrees of freedom become of importance in our calculations whenever a set of conditions are satisfied. These conditions are very similar to the criteria obtained by Oppenheimer[1] for the validity of electrodynamics.

Following the method introduced by Fermi, we shall expand the scalar potential V and the vector potential U in a Fourier series:

$$V = \Sigma_s Q_s(t) \cos \Gamma_s(x); \quad U = \Sigma_s U_s(t) \sin \Gamma_s(x).$$

If we substitute these expressions into the wave equations which the potentials satisfy,

$$\nabla^2 V - (1/c^2)(\partial^2 V/\partial t^2) = -4\pi\rho,$$

and

$$\nabla^2 u - (1/c^2)(\partial^2 U/\partial t^2) = -(4\pi/c)\dot{X}\rho,$$

we find $\ddot{Q}_s + 4\pi^2 \nu_s^2 Q_s = \rho_i \cos \Gamma_{si}$,

and $\ddot{U}_s + 4\pi^2 \nu_s^2 u_s = (\rho_i/c)\dot{X} \sin \Gamma_{si}$.

We now observe that the Dirac theory requires that $(dX_i/dt) = -c\gamma_i$. Thus the terms in the Hamiltonian which depend on the value of the potentials at the position of the electron X_i, for example,

$$\rho_i \Sigma_s Q_s \cos \Gamma_{si}, \quad \Gamma_{si} = (2\pi\nu_s/c)(\alpha_s X_i + \beta_s)$$

will be a function of the X_i's satisfying the equations $(dX_i/dt) = -c\gamma_i$. A solution of these latter equations is hard to obtain. Schrödinger, however, has solved the case where the charge moves with uniform velocity. His solution is

$$X_i = a_i + c^2 p_i t/W - (h\eta_i^0/4\pi i)(e^{-2\pi i W t/h}/W),$$

where p_i is the operator $(h/2\pi i)(\partial/\partial X_i)$ and W is the energy. The first two terms represent a motion of the charge with uniform velocity v_i, the last term a vibration of the inner degrees of freedom. For values of W not greatly in excess of mc^2, $h\eta_i^0/4\pi$ is of the order of the Compton wavelength and the frequency W/h of the order of c^2. For the case where the potentials exist, this solution will still give us an idea of the dependence of X_i on the time provided V is sufficiently small. If we substitute this value for X_i into $\cos \Gamma_{si}$ we find that the $\cos \Gamma_{si}$ depends markedly on $(h\eta_i^0/4\pi)e^{-2\pi i W t/h}$ whenever ν_s is so large that $\nu_s h\eta_i^0/c$ is of the order of unity, i.e., ν_s is of the order of $c^2/4[1-(v/c)^2]^{\frac{1}{2}}$.

Although we cannot find a solution for X_i when the potentials are large, an approximation can be obtained. This indicates that $(h\eta_i^0/4\pi)e^{-2\pi i W t/h}$ becomes appreciably changed by the application of the electric intensity F on the charge for a time of the order of $1/c^2[1-(v/c)^2]^{\frac{1}{2}}$, whenever

$$F \geq (hc^3/2\pi e)/[1-(v/c)^2]^{\frac{1}{2}}.$$

These conditions which define the region in which the inner degrees of freedom influence our calculations, are very similar to the criteria obtained by Oppenheimer. He found that by neglecting all terms which did not satisfy the criteria $\nu \leq mc^3/e^2$ and $F \leq m^2c^4/e^3$, the theoretical expressions for x-ray production, e.g., were much improved. This suggests that perhaps in the expansions for the potentials $\cos \Gamma_{si}$ and $\sin \Gamma_{si}$ should be altered in such a way that they are independent of the inner degrees of freedom of the electron.

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January 29, 1935.

[1] J. R. Oppenheimer, Phys. Rev. **47**, 44 (1935).

The Width of the $K\alpha$-Lines from Gaseous Krypton

The krypton radiation was excited by an electron beam from a specially designed cathode-ray tube. The beam being focused to the $0.01 \times 4 \times 20$ mm Al window by means of a magnetic lens then entered a cylindrical chamber 5 mm in diameter and 25 mm long filled with krypton at atmospheric pressure. The direction of the electron beam was perpendicular to the axis of the chamber which was provided with a mica window at one end and whose diameter was adapted to the range of the electrons at a voltage of 100 kv.

By means of a double crystal spectrometer with calcite crystals, an ionization chamber filled with methyl bromide and an FP 54 amplification circuit the natural width of the Kr $K\alpha$-lines could be measured.

The full widths at half-maximum were found to be 4.86 ± 0.3 volts for $K\alpha_1$ and 4.15 ± 0.35 volts for $K\alpha_2$. These values are not corrected for the finite resolving power of the crystals. They can, however, be compared with the results of Allison's[1] measurements on the width of lines from elements between the atomic numbers 26 and 48 which also are not corrected for the finite resolving power. The Kr values fit within the limits of error the ones one obtains by interpolation of Allison's data. Thus there is, within 8 percent, no difference in the width of $K\alpha$-lines from a gaseous and a solid element in the neighborhood of the atomic number 36. One still might expect an influence of the physical state of the anticathode on the width of lines for lighter elements, especially in view of Parratt's[2] measurements on alloy targets.

A new Kr line, probably a spark line, was found at 977.6 X.U.

ERNST WILHELMY

Ryerson Physical Laboratory,
University of Chicago,
February 4, 1935.

[1] Allison, Phys. Rev. **44**, 63 (1933).
[2] Parratt, Phys. Rev. **45**, 364 (1934).

Proceedings of the American Physical Society

MINUTES OF THE PITTSBURGH MEETING, DECEMBER 27–29, 1934

THE 36th Annual Meeting (the 196th regular meeting) of the American Physical Society was held at Pittsburgh on Thursday, Friday and Saturday, December 27, 28 and 29, 1934, in affiliation with Section B—Physics—of the American Association for the Advancement of Science. The presiding officers were Professor R. W. Wood, Vice President of the Society, Professor J. W. Beams, Dr. J. A. Becker, Professor P. W. Bridgman, Dr. K. K. Darrow, Dr. H. G. Dorsey, Professor H. A. Erikson, Dr. W. E. Forsythe, Professor L. G. Hector, Professor L. W. McKeehan, Professor D. C. Miller, Professor Alpheus W. Smith, Professor H. C. Urey, Professor J. Valasek and Professor J. W. Woodrow. There were about five hundred physicists in attendance at the meeting. Sessions were held at both the Carnegie Institute of Technology and the University of Pittsburgh.

On Thursday morning there were four parallel sessions for the reading of contributed papers.

Annual Business Meeting. The regular annual business meeting of the American Physical Society was held on Thursday afternoon, December 27, 1934, in the Little Theater of the Carnegie Institute of Technology at two o'clock. The meeting was presided over by Vice President Wood. The Vice President had appointed Messrs. H. A. Barton and R. T. Cox to canvass the ballots for the officers of the Society. They reported the following elections for the year 1935:

President	R. W. Wood
Vice President	F. K. Richtmyer
Secretary	W. L. Severinghaus
Treasurer	George B. Pegram
Managing Editor—three-year term	John T. Tate
Members of the Council—four year term	G. Breit Karl K. Darrow
Members of the Board of Editors—three-year term	William V. Houston Robert S. Mulliken I. I. Rabi

The Secretary reported that during the year there had been 178 elections to membership. The deaths of 14 members have been reported; 24 have resigned and 84 have been dropped. The membership of the Society as of December 21, 1934 was as follows: 2055 members, 662 fellows, 6 honorary members, total 2723.

The Treasurer presented a summary of the financial condition of the Society. It was impossible to present a final report for the year at the Annual Business Meeting because the fiscal year ends on December 31st. The Treasurer's financial report will be audited, printed and distributed.

The Managing Editor stated his appreciation of the cooperation of the members of the Society in condensing their papers and writing them concisely so that it was possible to publish a considerably larger number of papers in the same number of pages as the year before. The Managing Editor no longer makes a report on the financial condition of the publications since this is done by the American Institute of Physics.

The joint session with Section B and the American Association of Physics Teachers was held on Thursday afternoon at two-thirty o'clock in the Little Theater of the Carnegie Institute of Technology. The presiding officer was Dean Henry G. Gale, Vice President of Section B. Professor R. W. Wood, Vice President of the American Physical Society delivered an address on *Some Unusual Optical Problems*. The Retiring Vice President of Section B, Dr. C. J. Davisson, presented a paper on *Electron Optics*. This paper was read by Dr. Karl K. Darrow because the author was not able to be present.

On Thursday evening there was a trip to the Gulf Research Laboratories.

Friday morning and afternoon were devoted to a symposium on *Heavy Hydrogen and Its Compounds*. The morning session dealt with the physical aspects of the problem and the speakers were (1) Professor R. C. Gibbs of Cornell Uni-

versity on *Interferometric Studies of Alpha-Lines of Hydrogen and Deuterium;* (2) Professor G. H. Dieke of Johns Hopkins University on *The Use of Deuterium in Spectroscopic Investigations of Molecules;* (3) Professor Otto Stern of the Carnegie Institute of Technology on *Magnetic Moment of the Deuton;* and (4) Dr. M. A. Tuve of the Department of Terrestrial Magnetism, Carnegie Institution of Washington on *Nuclear Reactions Produced by High Speed Deutons.* This meeting was presided over by Dr. Karl K. Darrow of the Bell Telephone Laboratories, Inc. The afternoon session was presided over by Professor Harold C. Urey of Columbia University and the papers dealt with the chemical aspects of the subject. The speakers were (1) Professor Herrick L. Johnston of Ohio State University on *Chemical Separation of the Isotopes of Hydrogen;* (2) Professor Hugh S. Taylor of Princeton University on *Deuterium and Reaction Kinetics;* (3) Professor John R. Bates, Doctors J. O. Halford, L. C. Anderson and R. D. Swisher of the University of Michigan on *A Study of the Deuterium Exchange Reaction Involving Acetone;* and (4) Dr. F. G. Brickwedde of the Bureau of Standards on *Ortho- and Para-Deuterium.*

On Friday at four o'clock the Physical Society joined with the American Mathematical Society at the Josiah Willard Gibbs Lecture in the Little Theater. The speaker was Professor Albert Einstein of the Institute for Advanced Study, Princeton, New Jersey. The attendance at this meeting was about five hundred which was the limit of the seating capacity of the auditorium.

On Friday evening the Physical Society and the American Association of Physics Teachers held a dinner in the Webster Hall Hotel. Professor R. W. Wood, Vice President of the Physical Society, presided. The after-dinner speakers were President K. T. Compton, Dr. K. K. Darrow, Dr. Paul D. Foote, Dean Henry G. Gale, Dr. L. O. Grondahl, Dr. Paul E. Klopsteg, Professor R. A. Millikan, Dean Frederic Palmer and Professor A. G. Worthing. There were three hundred and twenty-six present at the dinner which was perhaps the largest attendance at any of the dinners of the Society.

Saturday morning was taken up with four parallel sessions of contributed papers. Saturday afternoon at one-thirty o'clock there was a joint meeting with the American Mathematical Society for the reading of invited papers on *Group Theory and Quantum Mechanics.* Professor H. P. Robertson of Princeton University presided. The authors were (1) Professor E. Wigner of Princeton University on *Symmetry Relations in Various Physical Problems;* (2) Professor J. H. Van Vleck of Harvard University on *Some Applications of Group Theory to Non-Relativistic Problems;* and (3) Professor G. Breit of the University of Wisconsin on *Some Applications of Group Theory to Dirac's Relativistic Theory.*

At two o'clock on Saturday there was a joint meeting with the Acoustical Society of America. Professor D. C. Miller of the Case School of Applied Science presided at this session. The speakers were (1) Dr. Hallowell Davis of the Harvard Medical School on *The Electrical Phenomena of the Cochlea and the Auditory Nerve;* (2) Professor Vern O. Knudsen of the University of California on *The Absorption of Sound in Gases;* and (3) Dr. E. C. Wente of the Bell Telephone Laboratories, Inc., on *Some New Instruments of Acoustical Research.*

One of the important features of the meeting was the Annual Science Exhibition. This was wide in its scope and was unanimously praised by the physicists in attendance.

Meeting of the Council. At the meeting of the Council held on Thursday, December 27, 1934, fifteen candidates were transferred from membership to fellowship and sixty-three were elected to membership. *Transferred from membership to fellowship:* Carl D. Anderson, Richard M. Badger, Willard H. Bennett, Charles D. Hodgman, Louis P. Granath, M. Stanley Livingston, Lewis M. Mott-Smith, Harald H. Nielsen, M. L. Pool, J. E. Shrader, Shirleigh Silverman, K. J. Sixtus, H. F. Stimson, John Strong and Lauriston S. Taylor. *Elected to membership:* Harriet W. Allen, Hubert W. Allen, Luis W. Alvarez, Walter A. Barkas, Else Bassoe, William O. Bennett, Jr., Sue Avis Blake, Robert H. Boden, Weldon H. Brandt, Richard T. Brice, M. Vertner Brown, Arthur L. Bryan, D. F. Caris, James D. Cobine, Robert Cortell, Willard R. Crout, L. A. V. DeCleene, Joy F. Dillinger, Charles S. Draper, Pol E. Duwez, Ludwig Eckstein, Franklin N.

Entwisle, Samuel H. Evans, Charles H. Fay, Nathan Ginsburg, Donald H. Hale, Ralph E. Hansen, William R. Haseltine, Robert O. Haxby, Albert G. Hill, Allen L. King, Ronold W. P. King, Israel Liben, Joseph Magliozzi, Marvin M. Mann, Jr., Thomas Mariner, Dwight P. Merrill, Jacob Millman, H. Rees Mitchell, Louis A. Morrison, Frank O. Mortlock, Donald N. Packer, J. F. Payne, William C. Price, J. Reginald Richardson, Randal M. Robertson, Fred C. Rose, John E. Rose, H. Hewell Roseberry, W. M. Rust, Jr., Hervey J. St. Helens, Milo B. Sampson, J. H. Sawyer, Jr., Robert W. Smith, Carsten C. Steffens, Rose Stewart, Albert M. Stone, Charles V. Strain, Julian L. Thompson, Gregory S. Timoshenko, H. B. Vincent, Allyn B. White and Ralph A. Wolfe.

The regular scientific program of the Society consisted of ninety-six papers. Numbers 27, 31, 49, 63 and 95 were read by title. The abstracts of the contributed papers are given in the following pages. An *Author Index* will be found at the end.

W. L. SEVERINGHAUS, *Secretary*

ABSTRACTS

1. Nuclear Structure and the Negative Proton. E. C. WESTERFIELD AND W. B. PIETENPOL, *University of Colorado.*—The negative proton is discussed and the suggestion made that it may be much more fundamental to nuclear structure than has been hitherto supposed. The working assumption is that nuclei are constructed of protons, antons, and, in the main, of a minimum number of neutrons. (It is suggested that either naton or anton be adopted as a suitable name for the negative proton, and anton is employed in the present paper.) The possible structure of simple nuclei is suggested. For example, the stability of the alpha-particle is attributed to a structure consisting of an anton surrounded by three protons. A compact structural formula for nuclei is proposed in the form (n_p, n_a, n_n) where n_p is the number of protons, n_a the number of antons, and n_n the number of neutrons. When atomic nuclei are divided into four classes according to the scheme

Class I	A even, Z even
Class II	A odd, Z odd
Class III	A odd, Z even
Class IV	A even, Z odd

it is found that nuclei of Classes I and II may be constructed entirely of protons and antons, although paired neutrons are not excluded. Nuclei of Classes III and IV, on the other hand, may be constructed entirely of protons and antons together with a single neutron. According to Harkins, Classes III and IV comprise only about 1.8 percent of all known nuclei in the earth's crust, and this is considered possible evidence that nuclei containing single neutrons are relatively unstable. The known reactions of artificial transmutations and induced radioactivity are considered from the standpoint of this theory.

2. Electrolytic Separation of Polonium and Ra D. G. B. PEGRAM AND J. R. DUNNING, *Columbia University.*—By the use of a disk cathode spinning several thousand revolutions per minute, as used by Professor Colin J. Fink* for the deposition of other metals from extremely dilute solutions, polonium and Ra D can readily be very completely removed from solutions and separated from each other, even when the solutions contain various impurities. The rapidly spinning cathode method has been applied also to the deposition of other radioelements.

* Fink and Rohrman, Trans. Electrochem. Soc. **58**, 406 (1930).

3. The Capture, Stability and Radioactive Emission of Neutrons. J. R. DUNNING, G. B. PEGRAM AND G. A. FINK, *Columbia University.*—Measurements have been made of the number of neutrons from a Rn–Be source which are detected in an ionization chamber 25 cm distant when the source is placed in the center of solid spheres of a series of sizes, 7.6, 12.6, 20.5 and 25.7 cm in diameter. The fraction of the neutrons coming out of the 25.7 cm spheres was, approximately, for H_2O 0.38, for C (coal) 0.78, for Al 0.68, for SiO_2 (sand) 0.87, for Cu (shot) 0.55 and for Pb (shot) 0.75. 2 cm of lead was always in front of the chamber as a gamma-radiation shield. Estimates based on the mean free path of neutrons between nuclear collisions (Phys. Rev. **45**, 586 (1934)) indicate that the probability of capture can hardly be greater than 25 percent per collision and may well be less than 10 percent for most cases. The large mechanical energy transfer probably accounts for much of the reduction in number in cases of light nuclei, and the figures for the probability of capture will be correspondingly reduced. This disappearance of neutrons appears to be no more than is called for by capture in the production of artificial radioactive atoms, by transfer of momentum on impact and perhaps by loss of energy in excitation, without supposing the neutron itself to be disintegrated by nuclear impact. Attempts with a large highly sensitive chamber to find radioactive emission of neutrons resulting from neutron bombardment of P as reported by Curie-Joliot and Preiswerk (Comptes rendus **198**, 2089 (1934)) failed to indicate any effect; similarly for Al, Fe and Cu.

4. Metastable Nuclei Produced by the Hard Gamma-Rays from Radium B+C. LEE DEVOL, *University of Pittsburgh. (Introduced by Dr. A. E. Ruark.)*—A theory is given of the distribution in time of the impulses from a Geiger-Mueller counter due to activating radiation if that radiation produces metastable nuclei which, at a later time,

emit radiation capable of operating the counter. An aluminum walled counter and a counter with a wall of nickel enclosed in lead glass were exposed to the radiation from radium B+C after passing through 6.25 cm of lead. The distribution of the impulses in time indicates that, in each case, at least 10 percent of the discharges were due to a secondary radiation associated with a decay period of the order of 1/2 second. The aluminum counter, when exposed to x-rays, showed a random distribution of the impulses in time. No attempt was made to determine whether the effect is a manifestation of induced radioactivity or whether the disturbed nuclei return to their original state.

5. The Construction and Use of Geiger-Müller Counters. G. L. LOCHER, *Bartol Research Foundation of the Franklin Institute.*—A discussion of the construction and use of Geiger-Müller counters for cosmic rays, gamma-rays, ultraviolet light, and for charged particles is given, based on experiences had in constructing about 600 counters for various purposes. The majority of these were cosmic-ray counters with tungsten filaments and copper-oxide cathodes, filled with a mixture of argon and oxygen. Technique for making reliable counters is described, especially in regard to the treatment of the electrode surfaces and the choice of a suitable gas. It has been found that smoothness of the cylinder-electrode is of little importance, but that the wire must be very free from conducting points, including dust precipitated on it electrostatically while the tube is in use. Criteria and tests of the correct behavior of a counter are given. Some amplifying and recording circuits for counter arrangements are described. These include circuits for single and coincidence counters, the circuits used in the two recent stratosphere flights, a triple-double-double coincidence circuit used by C. L. Haines and the author for a special beta-ray spectrograph, and a triple-multiple coincidence circuit for investigating cosmic-ray showers.

6. Measurements of the Angular Distribution of Cosmic-Ray Intensities in the Stratosphere with Geiger-Müller Counters. W. F. G. SWANN AND G. L. LOCHER, *Bartol Research Foundation of the Franklin Institute.*—The results of preliminary examination of the records obtained during the recent flight of Dr. and Mrs. Piccard, and in the National Geographic Society-U. S. Army flight are presented. The records were made as follows: (a) Natl. Geog.-U. S. Army flight, 40,000 ft., 46 min. (b) Piccard flight, 53,000 ft., 2 hrs. 30 min. The apparatus consisted, in each case, of 16 triple-coincidence cosmic-ray telescopes, arranged at 0°, 30°, 60° and 90° to the vertical, and employed 178 counting tubes. In the Piccard flight, a double-coincidence "intensity-meter," using 13 counters, was also carried for measuring the un-directed cosmic-ray intensity. A continuous time-compass record provides a means of examining the azimuthal variation of intensity. Some significant results are as follows: (1) The vertical intensity at 40,000 ft. (Natl. Geog.-Army flight) is about 39 times the value at sea level. At 53,000 ft. (Piccard flight), it is about 60 times the sea-level value. (2) Whereas the horizontal intensity is negligible in comparison to the vertical, at sea level, it is about 20 percent of the vertical intensity at 40,000 ft., and about 50 percent at 53,000 ft. We believe this result shows a significant effect of the earth's magnetic field on the secondary charged particles which are responsible for at least part of the operation of the counters. (3) The integrated intensity-function, which would determine the ionization per cc in an ionization chamber, by rays that actuate the counters, increases with altitude several times less rapidly than does the actual ionization. We believe this result to be significant of the participation of nuclear entities of high specific ionization in the ionization produced in a closed vessel. (4) The counting rate in the horizontal direction is particularly free from the contribution of simultaneous non-collinear rays.

7. North-South Asymmetry of the Cosmic Radiation. THOMAS H. JOHNSON, *Bartol Research Foundation of the Franklin Institute.*—During a recent survey of the directional distributions of the cosmic radiation a series of observations was made at an elevation of 14,000 ft. in Mexico at latitude (geomagnetic) 29°N, which compared the northern and southern intensities in the plane of the meridian from six different zenith angles. The ratios of the difference of southern and northern intensities to the average of southern and northern intensities together with their probable errors are given in Table I and give definite evidence of greater southern intensities particularly at angles close to the horizon. A north-south effect of this general character finds a natural interpretation in the theory of the orbits of charged particles, particularly as developed by Lemaitre and Vallarta. The curvatures of the orbits are such that the earth casts a partial shadow above the horizon on the pole side of the observer.

TABLE I.

Zenith angle	6.4°	19.2°	32°
$2(I_s-I_n)/(I_s+I_n)$	$.011 \pm .0096$	$.030 \pm .0092$	$.050 \pm .0096$
Zenith angle	45°	57.8°	70.7°
$2(I_s-I_n)/(I_s+I_n)$	$.012 \pm .015$	$.049 \pm .019$	$.085 \pm .024$

8. An Electrical Method for the Non-Destructive Testing of Sodium-Filled Valves. W. R. KOCH, *Materiel Division, U. S. Army Air Corps, Wright Field.*—The exhaust valves of aircraft engines are made with hollow stems which are partially filled with metallic sodium to promote cooling. Since the alloy steels used have electrical resistivities of the order of ten times that of sodium the presence of the sodium within the stem cavity greatly influences the electrical properties of the valve. The resistance gradient along the valve stem is much lower at those portions which contain sodium than at the portions which are hollow or which are solid steel. By connecting the valve in an electrical circuit so that a current of fifty amperes flows along the length of the stem the potential distribution along the stem may be determined potentiometrically. The location and amount of the sodium is indicated by the position and extent of the low slope portion of the potential curve. On the basis of the internal diameter of the valve stem and the resistance gradient along the stem the cooling medium may be identified. The results obtained were verified by

actually opening rejected valves as well as by examining radiographs in those cases in which detectable shadows were cast by the sodium column.

9. The Failure of Ohm's Law at High Current Densities. ERNST WEBER, *Polytechnic Institute of Brooklyn.*—The concept of compressibility of the electron gas (Phys. Rev. **43**, 781 (1933)) is introduced into the equation of metallic conduction and leads to an explanation of the observed deviations from Ohm's law at extremely high current densities (P. W. Bridgman, Proc. Am. Acad. Sci. **57**, 131 (1922)). From the theory a value for the number of free electrons per unit volume can be deduced which is considerably (about 10^2) smaller than the number of atoms per unit volume. This theory may constitute the first access to this number. The result is the same if one uses the classical distribution law or Fermi's law of distribution-in-energy. It is interesting to note that the expression for the compressibility as derived from Fermi's statistics has as minimum almost the same value and exactly the same dependence on temperature as the classical statistics would show.

10. Measurement of the Dielectric Constant of Air at Radiofrequencies. L. G. HECTOR AND H. L. SCHULTZ, *The University of Buffalo.*—In the course of preliminary work on the effects of large electric fields on the dielectric constants of gases, the heterodyne beat frequency method of measurement has been developed and applied to the absolute measurement of the dielectric constant of air at 900,000 cycles per second. Application of modern high frequency technique in coupling the variable and constant frequency oscillators to the detector completely eliminates the tendency of the two oscillators to synchronize. Improvement in the stability of the variable frequency oscillator allows time for temperature equilibrium of the gas to take place and facilitates recording the beat note by means of a string oscillograph. The results indicate that the dielectric constant of air at 900,000 cycles per second is in close agreement with values taken at low frequencies and with direct current measurements. In 26 determinations of the quantity $(\epsilon-1)$ the maximum deviation from the mean is 0.019 percent and the average deviation is only 0.007 percent. Constant sources of probable error reduce the reliability of the result to about 0.1 percent on the quantity $(\epsilon-1)$. This appears to be superior to previously reported results by more than one power of ten.

11. On the Use of Radio Broadcast Carriers for Constant High Frequency Currents. H. L. SCHULTZ AND L. G. HECTOR, *The University of Buffalo.*—Many broadcast stations are now equipped with excellent temperature controlled crystal oscillators so that the constancy of frequency compares favorably with that attainable with laboratory equipment. Moreover, the better stations are equipped with continuously operating frequency deviation meters and in addition the frequencies are periodically checked against monitoring stations. The particular difficulty arising in the use of broadcast signals for measurement purposes resides in the presence of modulation on the carrier. A method for effectively removing modulation and delivering the carrier frequency or multiples of this frequency is described. Removal of the modulation is effected through a special type of amplifying circuit which delivers essentially equal pulses of power to a low loss resonant circuit regardless of the percentage of modulation through wide limits.

12. Space Charge in a Conducting Electrolyte. WILLIAM SCHRIEVER, *University of Oklahoma.*—A constant difference of potential of 9 volts was maintained between two copper electrodes at the ends of an 8 cm square 40 cm long column of 0.0024 N copper sulphate solution. The difference of potential between a small movable copper electrode and the cathode was measured for positions between 0.1 and 39.9 cm from cathode. For each such position a curve, showing the potential difference as a function of the time, was obtained, for times up to 15 minutes. From these curves another set of curves was made showing the potential of a point in the electrolyte as a function of its distance from cathode, time being constant. And from each such curve the space-charge at any desired point was calculated. Within the region investigated, the space-charge in the cathode-end of the column was *negative*, and that in the anode-end was *positive*. However, further consideration showed that *very close* to the cathode the space charge must have been positive and that *very close* to the anode it must have been negative. At 0.6, 1.9 and 4.0 cm from the cathode the space-charges at the end of 15 minutes were, respectively, -60, -5.5 and -1.8 all$\times 10^{-6}$ statcoulombs/cm^3. These space-charges require, respectively, an excess of one SO_4 ion in every 0.75×10^{13} such ions normally present, one in 7.8×10^{13} and one in 23×10^{13}.

13. Multiple Space Charge in Double and Triple Grid Tubes. EVERETT W. THATCHER, *Union College.*—The study of the effect of space charge on thermionic currents has been restricted mainly to those cases in which maximum density of electrons occurs in close proximity to the emitter. An investigation has been made of certain phenomena associated with space charge external to a grid which surrounds the cathode. One case in which this situation was used has been treated briefly in connection with studies of shot-effect (E. W. Thatcher and N. H. Williams, Phys. Rev. **39**, 486 (1932)). This paper reports a new effect, the essential feature of which is a negative plate current-emission characteristic. The conditions under which this phenomenon is observed are outlined. Results of experiments with double and triple grid tubes are summarized. In general, two points on the characteristic may be found for which the plate current is independent of small variations in emission, whether of a statistical or "functional" nature. An explanation is presented based on the interaction of multiple space charge. An application to the problem of high gain amplification is suggested.

14. Shot Effect and Thermal Agitation in an Electron Current Limited by Space Charge. G. L. PEARSON, *Bell Telephone Laboratories, Inc.*—The theories of both shot effect and thermal agitation in an electron current limited

by space charge have been worked out for some time (F. B. Llewellyn, Proc. I. R. E. **18**, 243 (1930)). Experimental verification, however, is difficult because of the presence of other disturbing effects and inability to determine accurately the amount of space charge. Such measurements have now been made and they support the theory in each instance. (1) Shot voltage is reduced by space charge, the reduction being proportional to $J(\partial I/\partial J)^2$ where J is the total electron emission and I is the space current. This reduction is in addition to that caused by a decrease in the internal impedance of the tube. (2) A thermal agitation voltage is produced in the internal impedance of the tube which is dependent upon the temperature of the cathode. Although this effect is in qualitative agreement with theory the measured value is even less than that predicted.

15. Effect of Electrostatic Field upon Rate of Vaporization. E. HUTCHISSON, *University of Pittsburgh.*—Worthing and his associates have found that an electrostatic field directed away from a solid metallic surface lowers its rate of vaporization. A field of approximately 2×10^6 volts/cm decreases the rate of vaporization of molybdenum at 1462°K to 1 percent of its value without the field. The return of vaporized atoms polarized by the field as calculated by Greibach from the kinetic theory of gases does not explain the effect. In this paper an approximate calculation is made of the rate of vaporization on the basis of a change in the binding forces of surface atoms of molybdenum in the presence of an electric field. It is assumed that the balance between the attractions and repulsions of the atoms may be roughly represented by a Morse function. In the presence of the field, ions tend to move out, thus decreasing the repulsion while the electron cloud moves in, increasing the attraction. Both effects tend to increase the binding of the surface atoms. Assuming the measured compressibility, heat of vaporization and a polarizability equal to the atomic volume determined by crystal structure measurements, a computed change in binding is obtained which is of the right order of magnitude to explain the above change in the rate of vaporization.

16. Contact Potential of Thoriated Tungsten. DAVID B. LANGMUIR, *Massachusetts Institute of Technology.*—The contact potential of thoriated tungsten has been measured for different values of surface coverage and temperature. The experimental tube consisted of three coaxial cylinders inside which were two filaments, one of tantalum and one of thoriated tungsten. High vacuum conditions were obtained by evaporating tantalum from the first filament to the walls during exhaust. The metallic coating so formed on the glass constituted the cylindrical electrodes, and except for the filaments and leads there were no other metal parts within the tube. With the tantalum filament as cathode, with the tungsten cold, the volt-ampere characteristic to the tungsten was obtained for different states of activation, other conditions being kept constant. The curves so obtained could be made to coincide by shifting parallel to the voltage axis, and the amount of this shift was taken as the contact potential. The logarithm of the emission from the filament at zero field is a linear function of the contact potential, but the slope is less than the theoretical value e/kT. This discrepancy can be in large part explained by the temperature coefficient, which was observed to be of the order of magnitude of $5k$.

17. The Relation Between Field Emission and Work Function of Liquid Mercury. L. R. QUARLES, *University of Virginia. (Introduced by J. W. Beams.)*—The dependence on the cathode work function of the breakdown field between a liquid mercury cathode and a spherical molybdenum anode has been investigated. The general method of determining the breakdown potential is that of Beams (Phys. Rev. **44**, 803 (1934)). The contact potential difference between the mercury and a hot platinum filament is measured by two methods. In the first the mercury is connected to an electrometer and the system charged to a definite voltage. It is then isolated and allowed to come to equilibrium by the passage of electrons from the filament, which gives a measure of the mercury-platinum contact potential difference. The other method consists in charging the system to different voltages and letting it discharge for a fixed time, thus obtaining thermionic characteristics of the platinum-mercury circuit. The displacement of these characteristics gives the variation of the contact potential difference. If the work function of the platinum is assumed constant these measurements give the variation of the mercury work function. Results have been obtained over a work function range of one volt, and, while the trend is that forecast by the Fowler-Nordheim equation, the fields, calculated on the assumption of a smooth surface, are much less than predicted.

18. Optical Properties of Sputtered Metal Films. J. B. NATHANSON AND H. S. SEIFERT, *Carnegie Institute of Technology.*—Semi-transparent copper films, each of variable thickness, were produced by sputtering in hydrogen. From the location of the observed interference fringes, and the assumed density and optical constants of copper in the bulk, the masses of the films were computed as previously reported for manganese and platinum (J. O. S. A. **23**, 388 (1933)). The computed masses of copper were several times greater than those determined by weighing, as previously found for platinum. A higher refractive index, or lower density (or both), are thus indicated for the films as compared with these constants found for the metal in the bulk. A higher refractive index for copper was found (1) from independent observations of the film thickness by means of the Michelson interferometer; (2) from polarimetric observations following the method of K. Försterling (Göttingen Nachrichten, p. 58 (1911)). The physical state of the platinum films seems to vary somewhat with aging, since the location of the interference fringes was found to vary slightly over a period of about twenty months.

19. Christiansen Light Filters. E. D. MCALISTER, *Division of Radiation and Organisms, Smithsonian Institution.*—The Christiansen filter is unique in that by a proper choice of liquid and glass (or fused quartz) it yields a narrow band of high transmission in any region of the visible, near ultraviolet, and near infrared. Previous publications have shown

the necessity of temperature control, have given the various combinations of suitable liquids and glasses, and have shown the advantages of a good optical arrangement. The purpose of the present paper is to point out a further precaution that is necessary for any exacting use of the filter. Some radiation is absorbed and warms the filter even when it is water-cooled. Due to poor heat conductivity a temperature gradient is soon established and the band of transmitted light widens. In sunlight the filters are entirely unsatisfactory unless metal vanes (aluminum) are placed through the body of the filter to carry off the absorbed heat. Transmission measurements of a six-inch diameter filter equipped with vanes show 83 percent of the transmitted energy (solar) is in a 250A band, 4 percent of shorter wavelength, and 13 percent longer. The transmission is 55 percent at the peak. The possibility of making these filters of two glasses is discussed.

20. A New Method of Making Extremely Thin Films.* J. D. HOWE AND E. M. PURCELL, *Purdue University.* (*Introduced by K. Lark-Horovitz.*)—The method mentioned recently (K. Lark-Horovitz, H. J. Yearian and E. M. Purcell, Phys. Rev. **45**, 123 (1934)) has been developed for general use. A hole in a metal plate is filled with a volatile solid and the surface polished. This slit is clamped to the bottom of a liquid air container in a high vacuum. The material to be deposited is evaporated and covers slit and opening with a continuous film of desired thickness. The slit is then placed into the apparatus for the investigation and on evacuating the volatile material evaporates leaving the thin film freely supported on the slit. As volatile material camphor and naphthalene have been used. Since camphor produces in some cases oxidation (copper is deposited as cuprous oxide), purest naphthalene is now being used only. To avoid contact of the film with the air a small container with naphthalene is placed, after depositing of the film, under the slit, slightly heated from the furnace below and another layer of naphthalene is deposited so that the film is protected from both sides. In this way, also, materials which oxidize easily can be investigated in thin layers.

* Grateful acknowledgment is made to the American Philosophical Society for a grant-in-aid of this research. K. L. H.

21. Fluorescence of the Chlorophyll Series: Fluorescence and Photodecomposition in Solutions of Pheophorbide *b* and Methyl Pheophorbide *b*. H. V. KNORR AND V. M. ALBERS, *Kettering Foundation, Antioch College.*—The fluorescence spectra of pheophorbide *b* and methyl pheophorbide *b* in solution in anhydrous acetone have been photographed by a method previously described (Phys. Rev. **43**, 379 (1933)). The fluorescence spectrum of pheophorbide *b* consists of an intense band with its maximum at 650 mμ and a weaker band with its maximum at 678 mμ. As photodecomposition proceeds, the relative intensities of the individual bands vary considerably. The intensity of the longer wavelength band decreases to almost zero after one hour of irradiation. The appearance of an additional band was observed after fifteen minutes of irradiation. Its intensity increases during the first two hours and then decreases slowly. Its maximum is at 654 mμ. Three bands of almost equal intensity were observed in the fluorescence of methyl pheophorbide *b*, with maxima at 686, 651 and 640 mμ, respectively. The intensity of the 686 mμ and 640 mμ bands decreases to almost zero, after eight hours of irradiation. An additional band, with its maximum at 654 mμ, was observed. Its intensity increases during the first eight hours exposure to the radiation and then decreases. The band located at 654 mμ is also observed in the fluorescence of chlorophyll *b*.

22. The Luminescence of Frozen Solutions of Certain Dyes. FRANCES G. WICK AND CHARLOTTE G. THROOP, *Vassar College and Cornell University.*—Aqueous solutions of fluorescin are known to lose their luminescence suddenly when the water freezes. Frozen solutions of the uranyl salts are strongly fluorescent. Experiments described in this paper show the effect upon luminescent solutions of certain DuPont dyes of freezing the solutions and lowering the temperature to that of liquid air. Water, alcohol, acetone and glycerine were used as solvents. Ultraviolet light from a Westinghouse "black bulb" lamp was focused upon a glass tube containing the specimen. This tube was placed in a metal holder with a window in it and lowered by steps into an unsilvered Dewar flask containing liquid air. The intensities of luminescence at definite temperatures were measured by a Leeds and Northrup optical pyrometer with different color filters in the eyepiece to get the variation in intensity of definite wavelengths as the temperature was lowered. Marked changes take place in the intensity and color of the fluorescence and, in some cases, the frozen solutions are strongly phosphorescent. The abrupt variations which take place at certain temperatures may throw some light upon changes in the solvent at low temperature or upon the effect upon luminescence of the state of crystallization.

23. Interpretation of Anomalous Stark Intensities. J. S. FOSTER, *McGill University, Montreal.*—It is well known that the observed intensities of Stark components in the Balmer series are in many cases quite different from the relative probabilities of transition calculated by Schrödinger. Striking illustrations of such variations are afforded by the original experiments of Stark, the Lo Surdo analysis of $\overline{H_\alpha}$ by McRae, the extensive work by Mark and Wierl, the transition from typical canal-ray intensities to typical Lo Surdo intensities realized by Thornton, and the recent examination of Stark effects in the hydrogen isotopes by Foster and Snell. The present paper starts with the selective loss of initial states in collisions, as explained by Bohr. Appreciable development of this asymmetry in final states may be expected only under the most favorable circumstances, owing to their small size and low polarization. From the photographs (see Abstract, Foster and Snell) it is learned that dipole collisions are important, and it is assumed that the asymmetry is so transferred to the final states. Selective absorption follows as the simplest explanation of the experiments. If the field is not constant, one must not overlook the absorption of a photon by atoms up or down stream in a field different from that at the origin of the photon, but nevertheless capable of absorbing light of the wavelength and polarization characteristic of the light quantum. It appears, however, that this feature plays a

secondary role in the determination of observed relative intensities of Stark components in the majority of the experiments cited.

24. The Spectra of Lead IV and Bismuth V. G. K. SCHOEPFLE, *Cornell University.*—Early investigations in the spectra of Pb IV by Rao and Narayan, Smith, and Kishen have been extended to include 34 terms arising from the configurations $5d^{10}ns$, $5d^{10}np$, $5d^{10}nd$, $5d^{10}5f$, $5d^96s^2$, $5d^96s6p$ and $5d^96s6d$. With data by Arvidsson, Smith and the author, the region reported extends from 198 to 5005A, and 79 lines have been classified. In the extension to Bi V, values have been assigned to 14 terms involving 18 lines in the region below 1487A. By a Hick's formula the value of the $5d^{10}6s\ ^2S_{0\frac{1}{2}}$ term has been computed to be 340,885 cm^{-1} for Pb IV and 451,700 cm^{-1} for Bi V, giving ionization potentials of 42.0 volts and 55.7 volts, respectively.

25. Relative Transition Probabilities of Almost Closed Shells. C. W. UFFORD, *Allegheny College.*—The method of calculating the relative transition probabilities of different multiplets in Russell-Saunders coupling from spectroscopic stability has been simplified for configurations involving almost closed shells, so that transition probabilities for these configurations may be calculated as easily as those for the configurations containing the electrons missing from the almost closed shells. First it has been shown that the transition probabilities are the same for two pairs of configurations which are the complements of one another. The complementary configuration is the one obtained when all electrons outside closed shells are replaced by the electrons missing from the closed shell of which they are a part. Thus the transition probabilities for the configurations $d^5p^5-d^7p^5$ are equal to those for d^2p-d^3. To calculate the transition probabilities for configurations containing almost closed shells, it is necessary to write the zero order states of but one configuration, choosing from the LSM_LM_S states the one with the fewest terms. In writing the zero order states the almost closed shells are represented by the quantum numbers of the electrons missing from the shell. By this method the relative transition probabilities of different multiplets have been calculated for the transitions $d^9p-d^8p^2$, $d^9p^2-d^8p^3$, $d^8p-d^7p^2$, and $d^7p-d^6p^3$.

26. The Fundamental Band of H^3CN at 17.5 μ. PAUL F. BARTUNEK AND E. F. BARKER, *University of Michigan.*—The fundamental band of heavy hydrogen cyanide H^3CN has been measured with a spectrometer having a grating with 1200 lines per inch and a KBr fore prism. There is a strong zero branch at 570 cm^{-1} and the fine structure lines on each side are well separated. From the line spacing the moment of inertia of the molecule may be computed, neglecting interactions. Its value is approximately 23.1 $\times 10^{-40}$ g cm^2. A comparison of the number with the corresponding value for ordinary hydrogen cyanide permits the calculation of the internuclear distances.

27. The Structure of Rhombic Sulphur. B. E. WARREN AND J. T. BURWELL, *Massachusetts Institute of Technology.*—From rotation and oscillation photographs with Mo $K\alpha$, rhombic sulphur is found to have the following cell and space group: $a=10.48$A, $b=12.92$A, $c=24.55$A, $Z=128$, space group V_h^{24} ($Fddd$). The structure contains S_8 molecules which are symmetrical puckered rings with S–S distance 2.12A and bond angle $\alpha=105°$. The atomic coordinates are determined by comparison of calculated amplitudes with visual intensity estimates from oscillation photographs. The relation of rhombic sulphur to the high temperature forms is discussed briefly.

28. The Determination of the Components of Interatomic Distances in Crystals. A. L. PATTERSON, *Massachusetts Institute of Technology.*—In a previous communication (Patterson, Phys. Rev. **46**, 372 (1934)) it has been shown that a Fourier series can be set up which represents the weighted average electron distribution about any point in a crystal. The coefficients in this series are the quantities $F^2(hkl)$ obtained from absolute measurements of intensity. The coordinates of its maxima then represent in direction and magnitude the atomic distances in the crystal. A new series has now been derived which represents approximately a similar average distribution of atom centers. The coefficients of this series are $F^2/\bar{f}^2$ where $\bar{f}=\Sigma f_i/\Sigma Z_i$; the summations extending over all atoms of the cell. f_i is the atomic scattering factor at absolute zero for the i-th atom whose atomic number is Z_i. The f_i's and $\bar{f}$ are functions of $\sin\theta/\lambda$, θ being the Bragg reflection angle of the plane (hkl) for radiation of wavelength λ. The peaks of the new series are much sharper than before and greater resolution can therefore be obtained. There is some distortion owing to the incompleteness of the new series and the compromise involved in the use of the factor $\bar{f}$; but this is apparently small. Copper sulphate pentahydrate is used as an example; the calculations being based on part of the data recently published by Beevers and Lipson.

29. A Glassy State of Arsenic. W. E. MCCORMICK AND WHEELER P. DAVEY, *Pennsylvania State College.*—It is found that below 100°C arsenic vapor condenses in pure hydrogen to give an amorphous (to the x-rays) powder of very small particle size. When the vapor is condensed between 100°C and 130°C a mixture of powder and coherent sheet is obtained. Between 130°C and 250°C only the coherent sheet is obtained. The metallic luster of the sheet increases with the temperature of condensation. X-ray examination shows the deposit to be non-crystalline. It might be described as a metallic glass. Above 250°C the deposit has slightly less luster and is distinctly crystalline to the x-rays. It is believed that this is the first report on the existence of three types of solid (amorphous flour, glass, crystal) for a single metal. References for related work: Strumanis (Zeits. f. physik. Chemie **B13**, 316 (1931)) on *rate* of crystal growth of Zn and Cd; Ingersoll and DeVinney (Phys. Rev. **26**, 86 (1925)) on amorphous nickel films; Bettendorf (Ann. d. Chemie **144**, 110 (1867)) on what he called (without experimental evidence) "amorphous arsenic" (probably the flour).

30. Electron Diffraction by Transmission Through Thin Silica Glass Films. LOUIS R. MAXWELL AND V. M.

MOSLEY, *Bureau of Chemistry and Soils.*—Electron diffraction has been obtained by the transmission of electrons (25 to 38 kv) through thin films of silica glass. The films were obtained from the glass after blowing out into a thin walled bubble. Further reduction in the thickness of the film was made by treatment with hydrofluoric acid. The interference pattern recorded on a photographic plate can be described as follows: (1) at small angles the electron scattering was strong in contrast to the known x-ray photographs which show small scattering in this region, (2) the prominent ring at $(1/\lambda)\sin\theta/2=0.12$ commonly observed by x-rays was present, (3) at $(1/\lambda)\sin\theta/2$ equal to about 0.20 a prominent halo was observed, (4) a strong diffuse ring appeared at $(1/\lambda)\sin\theta/2=0.40$. These results can be discussed from the standpoint of scattering from amorphous SiO_2 previously treated by Warren (Phys. Rev. **45**, 657 (1934)). Frequently sharp interference spots or partially completed circles characteristic of crystal formation were found in addition to the above pattern. The most prominent ones give Bragg spacings of 4.2A (strong), 3.7A (strong) and 2.52A (weak). The origin of this pattern has not been definitely established and it is possible that it may arise from impurities.

31. Depth of Penetration of Electrons Diffracted by Single Crystals. H. E. FARNSWORTH, *Brown University.*—A known number of atom layers of one metal were deposited on the surface of a single crystal of another metal by evaporation in a high vacuum. Direct results on depth of penetration were obtained from measurements on electron diffraction as a function of the thickness of the surface layer. A silver film deposited on a copper crystal is amorphous. A layer one atom deep reduces the maxima of the beams from the copper lattice by at least 70 percent for energies up to 300 e. volts. A number of foreign silver atoms equal to a few hundredths of that contained in one atomic layer can be detected by this method. A silver film deposited on a gold crystal is crystalline. The surface atomic layer of silver contributes at least 50 percent to the maxima of beams from a thick crystal for energies up to 300 e. volts, while a surface layer two atoms deep contributes at least 90 percent. This predominating effect of the surface atomic layer for primary energies as high as 300 e. volts is not in accord with theoretical predictions of v. Laue.

32. Intensity Distribution in Electron Diffraction Patterns. K. LARK-HOROVITZ, H. J. YEARIAN AND J. D. HOWE, *Purdue University.*—With the method described above* electron diffraction patterns of thin layers of bismuth, cadmium, calcium hydroxide, copper, cuprous oxide, gold, sodium nitride, nickel, tungsten oxide, zinc, zinc oxide and zinc sulfide have been obtained using cathode rays from a gas discharge of 50–80 kv. The intensity distribution is discussed as a function of (a) surface condition of the crystallites, (b) refraction of the electron waves, (c) orientation, (d) atom factor. In all cases mentioned "forbidden" orders have been found which in some cases exhibit an extremely sharp diffraction pattern. Their relation to refraction, inner potential and surface layers is being discussed. *The values of sin θ/λ for the forbidden inner rings are the same for Au, Ag, Cu, Cu_2O, Ni, Cd.*†

* See Abstract 20. † See reference to Abstract 20.

33. Triatomic Ions in Mixtures of the Hydrogen Isotopes. OVERTON LUHR, *Union College.**—A mass-spectrograph analysis has been made of aged ions in mixtures of hydrogen and deuterium. The concentration of deuterium varied from more than 80 percent to less than one percent. After drifting through 5 cm of gas at about 0.5 mm pressure, the ions were found to be over 95 percent triatomic; that is, H_3^+, H_2D^+, HD_2^+ and D_3^+. Measurement of the relative intensities of the triatomic ion peaks indicates a slightly greater number of H_3^+ and D_3^+ ions compared to H_2D^+ and HD_2^+ than would be expected from probability considerations if the H and D atoms behaved exactly alike. This apparent tendency for like atoms to group together would be expected from the equilibrium constants for the different types of molecules in the gas mixtures employed. Consideration of the probabilities of formation of the various triatomic ions, combined with measurement of the relative intensities of the peaks, furnishes a convenient method for analyzing a given sample of gas to determine the abundance of the isotopes. Certain precautions must be observed in the application of the method.

* Experimental work performed at Massachusetts Institute of Technology.

34. A New Ion Source for Mass Spectroscopy. A. J. DEMPSTER, *University of Chicago.*—Spectrum analysis has shown that multiply-ionized atoms of a great many elements are formed in "hot-sparks" and in high frequency electrodeless discharges. It has been found that a small spark at a pressure of 10^{-6} mm excited by high frequency alternating current from a Tesla coil is a source of multiply-charged ions which may be detected by the methods of positive ray analysis. In preliminary experiments the ions were accelerated by a potential of 20,000 volts and analyzed by the parabola method with electric and magnetic deflections at right angles to each other. With a spark between steel and tungsten, sixteen different ions were found including hydrogen, tungsten, carbon with one to three charges, and iron with one up to six charges. Exact atomic weight comparisons of these ions are planned with a new mass spectrograph of large resolving power.

35. A Proposed Mass Spectrograph. W. B. PIETENPOL, *University of Colorado.*—A new type of mass spectrograph is described, embodying two energy selectors of the cylindrical-condenser type employed by Aston, and a velocity selector of the balanced field type used by Bainbridge. The advantages claimed for the proposed instrument are 180 degree deflection giving large dispersion, both direction and velocity focusing, normal incidence, and a linear mass scale. The instrument is so designed that the energy of the ions selected by the first energy selector varies automatically with the initial energy imparted to the ions, so that a maximum effect may be obtained for all masses. The relative effect is therefore proportional to the relative abundance. Since the design of the instrument places rather nar-

row limits on the range of spectrum which can be photographed at a given setting, it is proposed to employ an electrometer alternatively with a photographic plate for general use. Because of its large dispersion, and the linear relation between the electric field employed and the specific charge of the ion selected, the proposed instrument seems particularly well adapted to bracketing methods of determining isotopic weights.

36. Some Unusual Optical Problems.* R. W. Wood, *Johns Hopkins University*, Vice President of the American Physical Society.

37. Electron Optics.* C. J. Davisson, *Bell Telephone Laboratories, Inc.* Address of the Retiring Vice President of Section B—A.A.A.S.

38. Interferometric Studies of Alpha Lines of Hydrogen and Deuterium.* R. C. Gibbs, *Cornell University.*

39. The Use of Deuterium in Spectroscopic Investigations of Molecules.* G. H. Dieke, *Johns Hopkins University.*

40. Magnetic Moment of the Deuton.* Otto Stern, *Carnegie Institute of Technology.*

41. Nuclear Reactions Produced by High-Speed Deutons.* M. A. Tuve, *Department of Terrestrial Magnetism, Carnegie Institution of Washington.*

42. Chemical Separation of the Isotopes of Hydrogen.* H. L. Johnston, *Ohio State University.*

43. Deuterium and Reaction Kinetics.* H. S. Taylor, *Princeton University.*

44. A Study of the Deuterium Exchange Reaction Involving Acetone.* John R. Bates, J. O. Halford, L. C. Anderson and R. D. Swisher, *University of Michigan.*

45. Ortho- and Para-Deuterium.* F. G. Brickwedde, *Bureau of Standards.*

46. X-Ray Spectra and Chemical Combination. Joseph Valasek, *University of Minnesota.*—The x-ray target described by the writer (Phys. Rev. **43**, 612 (1933)) has been modified by cutting away its surface so that the primary x-rays from the face of the target do not enter the spectrograph. This removes the principal source of contamination of the spectra. Compounds not readily available as single crystals are pressed into a "pill" of semi-circular form which is used as the source of secondary x-rays. The $K\beta$ lines of the sulphides and chlorides of some of the elements in columns one and two of the periodic table have been measured. No regularities were apparent. In the cases of S, FeS_2 and ZnS, it was found that different crystal modifications of the same compound give the same spectrum as far as could be observed. The form of tube described lends itself readily to chemical analysis.

47. The Crystal Structure of Beta-Manganese. Thomas A. Wilson, *Union College.*—Extension of previous work in applications of mathematical crystallographic methods to powder x-ray data of the manganese system has resulted in the complete solution of the beta-manganese structure. The structure is cubic; the space group is O_h^6; the cube edge length is 12.58A; the cube content is 160 atoms, arranged in the following groups of equivalent positions according to the Wyckoff tabulation: 8*a*, 8*b*, 48*e*, and 96*i*, with $u=0.11$ in 48*e*, and $u=0.10$, $v=0.33$ in 96*i*. These parameters have been checked by intensity calculations using structure factor values based on the Thomas atomic model. The x-ray density of beta-manganese is calculated to be 7.29.

48. Comparison by X-Ray Diffraction of *p*-Azoxyanisol in Liquid and Liquid Crystalline Phases. H. R. Letner and G. W. Stewart, *University of Iowa.*—It is found that the intensity at the peak of the diffraction curve is five percent greater for the liquid crystalline phase than for the liquid and is displaced about 0.2° with Mo $K\alpha$ radiation. Observations require precautions against convection currents which may lessen the intensity in the former phase. The diffraction curves for the two are otherwise strikingly alike from 0° to 40°. The differences may be in liquid structure as well as in stability, which is certainly greater in at least two dimensions for the liquid crystal. Observations were compared at 125° and 150°C. The change of peak intensity is contrary to the findings of Katz but the change in diffraction angle agrees.

49. Shapes and Wavelengths of *K* Series X-Ray Lines. C. H. Shaw and J. A. Bearden, *National Research Fellow, Cornell University; Johns Hopkins University.*—The shapes and wavelengths of the principal lines of the *K* series of elements Ti 22 to Ge 32 were determined by means of a Societe Genevoise double crystal spectrometer. The calcite crystals used showed resolving power close to the theoretical value throughout the range of wavelengths studied. The targets were of electroplated metal wherever possible to insure a high degree of purity. The widths at half maximum and the index of asymmetry were measured in the (1−2), (1+1) and (1+2) positions. In general it was found that the measurements in the various orders were different. In the case of the widths a calculation of the resolving power explains the difference. Curves of the variation of width and asymmetry with atomic numbers are given. Attention is called to the fact that even though gallium was in the liquid state the points lie on the curves. Thus the shape of the line may be said to be independent of the state. Diffraction angle measurements were made in both the first and second orders. The precision circle on which the second crystal was mounted was calibrated every five degrees to 0.2″ of arc by means of the four microscope method. The two determinations of wavelength always agreed to about 0.001 percent, which somewhat exceeds previous photographic results in

* Invited papers.

accuracy. The wavelength, width and relative intensities of certain satellites accompanying the β_1 and β_5 lines were also measured.

50. On X-Ray Line Shapes and the Double Crystal Spectrometer. LLOYD P. SMITH, *Cornell University.*—In a previously reported analysis of the double crystal spectrometer, a method for determining the x-ray line shapes for any pair of crystals was given. This required rocking curves in the (1, +1), (1, +2), (2, +1) and (2, +2) orders. A criterion based upon information supplied by the (1, −1) and (1, +1) rocking curves has been deduced which allows one to ascertain beforehand whether the method mentioned above has to be applied to obtain the true line shape or whether the (1, +1) rocking curve is itself the line shape within experimental error.

51. X-Ray Intensity Measurements with a Geiger-Müller Counter, and the Determination of the Structure Factor for KCl. DONALD P. LEGALLEY, *The Pennsylvania State College.*—A special Geiger-Müller counter has been developed which responds reliably to x-rays from a molybdenum target. The amplified impulses from this counter are recorded mechanically with the aid of a thyratron circuit. Oscillograph records taken by discharging the counter very rapidly with radon show a time of recovery of less than 0.001 sec. Therefore for counting rates up to 600 per minute there is less than a 1 percent correction due to random impulses. The counter and the circuit have been used to measure the intensity of the Mo *K*-alpha beam diffracted by the planes of finely powdered KCl, as well as the intensity of the undiffracted beam. (Balanced filters were used.) In this way the ratio of the intensity of the diffracted beam to the intensity of the main beam P_S/P_0 is measured, and when used in the well-known equations

$$F^2=\frac{2Qm^2c^4\sin 2\theta}{n^2\lambda^3e^4(1+\cos^2 2\theta)};\qquad \frac{P_S}{P}=\frac{Qfl\rho'h}{4\pi r\rho\sin 2\theta}$$

gives a value for the structure factor F. The structure factor for the (100) planes of KCl has been determined to be 33.4 ± 2.2. Further work on NaCl, Fe and W is in progress.

52. X-Ray Diffraction and the Fatigue of Metals. CHARLES S. BARRETT, *Carnegie Institute of Technology.*—Some preliminary results of an extended x-ray diffraction study of the fatigue process in various alloys are as follows: The radial widening of Debye lines is relatively insensitive to changes in the metal brought about by fatigue; in fact, an aluminum alloy (25 ST) shows no detectable widening of this type and a silicon steel shows only a minute amount although both had received more than 10^7 reversals of stress just below the endurance limit. On the other hand a sensitive detector of changes during fatigue is the peripheral widening of spots in Debye rings, or the equivalent asterism. With the unbroken steel specimen mentioned above, the spots from highly stressed areas are much broader than those from slightly stressed areas, while areas at a given stress level give similar spots. Photograms of various areas on broken surfaces of fatigue specimens vary somewhat but always exhibit extreme widening.

53. The Connecting Link between Classical Electromagnetic Theory and Wave Mechanics *via* a Derivation of the Schrödinger Equations as a Boundary Value Problem on the Atom. LLOYD T. DEVORE, *Pennsylvania State College. (Introduced by W. R. Ham.)*—Arguments are presented to show that the atom may be visualized as having a finite shell for an outer boundary and no external field (neutral). It is also argued that if a Coulomb field exists between the charges within the atom, the picture necessarily represents a dynamic model (Earnshaw's theorem) and in particular the charges must be accelerated. With this picture as a basis, the following assumptions are fundamental to the derivations: (1) The vector potential of the field set up by the accelerated charges vanishes at the nucleus and at the outer boundary of the atom. (2a) The field set up within the atom may be quantized by an application of the quantization rule $\int p dq = nh$. (2b) An alternative assumption to that expressed in (2a) is the familiar relation $E=h\nu$, where E is the energy associated with the standing electromagnetic waves within the atom and ν their frequency. (3) The law of the conservation of momentum may be applied to obtain relationships between the electromagnetic field and mechanical motions within the atom. With the above assumptions, the Schrödinger equations:

$$\Delta\psi+(8\pi^2m/h^2)(E-V)\psi=0, \qquad (1)$$
$$\Delta\psi-(8\pi^2m/h^2)V\psi+(4\pi im/h)(\partial\psi/\partial t)=0, \qquad (2a)$$
$$\Delta\bar{\psi}-(8\pi^2m/h^2)V\bar{\psi}-(4\pi im/h)(\partial\bar{\psi}/\partial t)=0 \qquad (2b)$$

are derived by starting with the equation satisfied by the vector potential within the atom.

54. Equation of Waves in Media with Velocity Varying with Time. P. I. WOLD, *Union College.*—The equation of a wave in a medium in which the velocity is a function of time has been obtained. The most convenient time function to handle appears to be $c=c_0e^{-\alpha t}$ and the equation obtained is $y=a\sin 2\pi\nu_0(t-(1/\alpha)\ln\zeta)$, where ν_0 is the frequency at the source and $\zeta=1+(\alpha x/c_0)e^{\alpha t}$. This equation gives a redward shift in light frequency proportional to the distance of the observer from the source. The differential equation which is satisfied by this is

$$(\partial^2y/\partial t^2)+\alpha(\partial y/\partial t)=c_0^2e^{-2\alpha t}(\partial^2y/\partial x^2).$$

55. A Theoretical Discussion of Professor Miller's Paper[1] on the Ether Drift Experiments. W. B. CARTMEL, *Westmount, Quebec, Canada.*—This investigation led to a redevelopment of the equations of Lorentz,[2] and on taking into account the mirror angle ω which Lorentz did not do, these equations gave for the fringe shift:

$$\delta F=\frac{l}{\lambda}\left[2\sqrt{2}\omega\frac{v}{c}\cos\left(\theta-\frac{\pi}{4}\right)+\frac{v^2}{c^2}\cos 2\theta\right], \qquad (1)$$

which is similar to an equation given by Hicks.[3] From Eq. (1) curves have been drawn which fit remarkably well with Miller's results, but the value it gives for the earth's

velocity v is wrong. Further consideration from the viewpoint of standing waves led to the equation:

$$\delta F=\frac{l}{\lambda}\left[\omega\frac{v^2}{c^2}+\frac{1}{2}\frac{v^2}{c^2}\cos\theta+\omega\frac{v^2}{c^2}\cos 2\theta+\frac{1}{2}\frac{v^2}{c^2}\cos 3\theta+\omega\frac{v^2}{c^2}\sin 2\theta\right]. \quad (2)$$

Eq. (2) shows (1) From Miller's results or from the Michelson-Morley results,[4] a value for the orbital component of the earth's velocity of roughly 30 km per second. (2) Since the terms in 2θ are functions of the mirror angle ω, no v^2/c^2 effect can be expected with a flat field instead of fringes, which explains the negative result of Kennedy[5] and Illingworth,[6] who only looked for the v^2/c^2 effect. (3) Fourier components identical with those given on page 227 of Miller's paper.[1] (4) A curve which fits Miller's results within a hundredth of a fringe.

Most important of all, the considerations that led to Eq. (2) also gave the Lorentz transformation without having to assume a contraction of the interferometer arm, but Miller's results are not found to be in agreement with principle I of the special theory of relativity. Curves will be presented that show clearly that Eq. (2) fits Miller's results much better than Eq. (1), and a complete derivation of the formulas will be given.

[1] Dayton C. Miller, Rev. Mod. Phys. **5**, 203 (1933).
[2] H. A. Lorentz, *The Theory of Electrons*, 178 (1916).
[3] W. M. Hicks, Phil. Mag. **6**, 3, 32, 555 (1902).
[4] A. A. Michelson and E. W. Morley, Phil. Mag. **5**, 24, 449 (1887).
[5] R. J. Kennedy, Astrophys J. **68**, 367 (1928).
[6] K. K. Illingworth, Phys. Rev. **30**, 692 (1927).

56. A Modification of the Heitler and London Method. CLARENCE ZENER, *The Institute for Advanced Study, Princeton, N. J. (Introduced by W. L. Severinghaus.)*—The customary Heitler and London method starts out from atomic wave functions for the electrons. The orbital method of Hund and Mulliken uses solutions of a two center field in first approximation. A combination of the two is proposed in which atomic wave functions are used modified by the neighboring atom. Such wave functions are obtained by starting the Hartree self-consistent field with atomic in place of molecular orbital wave functions. In this way the gradual transition, as the interatomic distance decreases, from the atomic to the molecular functions is followed through. When this method is carried out it may be possible to avoid the large repulsive interactions between the valence electron of one atom and the inner shell of the other atom, which have recently been found by James.

57. The Theoretical Binding Properties of Metallic Lithium. FREDERICK SEITZ, *Princeton University.*—On the basis of previous theoretical developments concerning the binding properties of metals, and applied in detail to sodium, an investigation of the constitution of lithium is undertaken. In the previous work the process of solution was divided into two parts, namely, the solving of the best one-electron approximation on the one hand, and the investigation of more general statistical correlations of electron-positrons than those afforded by the first part, on the other. In the case of Na, the first part yielded about one-fifth of the observed binding energy while the second, for which the most satisfactory treatment has been given by E. P. Wigner in a very recent paper, removes about 80 percent of the remaining discrepancy. In the case of Li, it is found that the one-electron picture is appreciably changed, the individual wave functions being less similar to free-electron wave functions than in the case of Na. This has as its consequence that almost half of the observed energy is included in the one-electron solution. At the present stage of calculation, the result of Wigner on the nature of additional correlations is taken over directly and yields a binding energy of 34 kg Cal. as compared with the observed value of 38.9.

58. Magnetic Moments of the Deuton and Other Nuclei. D. R. INGLIS, *University of Pittsburgh.*—It is shown that the magnetic and mechanical moments of nuclei (except the deuton) can be correlated in terms of the moments of the particles (protons with gyromagnetic ratio $g=-5$, neutrons with $g=-1.1$) in excess of the number giving (empirically) no moment: that is, one proton or neutron with a possible "orbital" moment and perhaps two more neutrons with only spin moment. The approach is somewhat similar to that of Landé-Tamm-Altschuler, but is simpler in number of vectors, introduces the importance of the proton-neutron bond, finds that states of lowest proton spin-orbit coupling energy fit the data best, and explains the accurately known data (ratios) without contradiction. The deuton is taken to be a simple rotator, proton and neutron. It should be stable in its zero-rotation state, but then the spins with the above g's would give a much larger value than the deflection value $|g|=0.7$ for the deuton. If we assume an unexplained stability of the first rotational state (a similar suggestion has been made in comparing the mass defects of the deuton and alpha-particle), solution of a secular problem leads to a sufficiently small value of g for the deuton. With only a dipole spin-spin coupling, the value is $\frac{1}{2}$. Assuming magnetic spin-spin and rotation-spin coupling (including the Thomas relativistic correction, the factor being $\frac{3}{4}$ in this case) we get $g=-0.6$.

59. Nuclear Spin in Isotopic Mixtures. I. I. RABI, *Columbia University.*—It is pointed out that nuclear spins and magnetic moments of the different isotopes of a mixture can in some important cases be measured by means of atomic beams. The method utilizes the fact that the different isotopes when they have different magnetic moments or spins have some magnetic levels which have zero moments at definite values of the external magnetic field. This method also offers an independent measure of the relative abundance of the isotopes which possess nuclear magnetic moments. The case of $i=\frac{1}{2}$ however requires separate discussion.

60. The Shoal Fathometer. HERBERT GROVE DORSEY, *U. S. Coast & Geodetic Survey.*—The Shoal Fathometer, a special case of the fathometer described in the J.O.S.A. and R.S.I., Sept. 1924, was recently developed at the U. S. Coast & Geodetic Survey as a precision instrument for measuring shallow depths. A 1025 cycle tuning fork drives

a synchronous motor at 20.5 revolutions per second and the scale is graduated to 20 fathoms making the velocity of calibration 820 fathoms per second. Instead of using the flash in a rotating neon tube for visual indication, a thin aluminum disk with a narrow slot is rotated in front of a large neon tube bent in a circle. The echo flashes the entire tube by condenser discharge through a thyratron and the slot appears to stand still, indicating the depth. A magnetostriction transceiver is actuated from a 17,000 cycle thermionic generator, by light reflected on a photoelectric tube each revolution, causing a condenser to discharge through a thyratron, keying the tubes to produce a short signal in the water. There are no moving contacts in any part of the system. In actual use the indications seem more reliable than the standard method of measuring depths by a line and lead sinker. A complete description will appear in the *Review of Scientific Instruments.*

61. Optical Observations of Sound Waves in Arcs. C. G. SUITS, *General Electric Company.*—Sound waves passing through atmospheric pressure arcs are photographed with a rotating mirror camera of $\frac{1}{2}$ microsecond time resolution. The method is analogous to that employed in studying exploded wires by Anderson and Smith (Astrophys. J. **64**, 359 (1926)). The sound source employed is a condensed discharge through a 0.003″ iron wire placed 5 cm from and parallel to the axis of the 40 ampere white flaming arc between cored carbons. A preliminary value for the sound velocity in this arc is 1.85×10^5 cm sec.$^{-1}$, from which the temperature is calculated (by a method described in a separate paper) to be 5300°K.

62. Sound Velocity in Gas Mixtures at High Temperatures. H. PORITSKY AND C. G. SUITS, *General Electric Company.*—Experimentally determined values of the velocity C of sound in atmospheric pressure arcs in air are interpreted in terms of the temperature of the gas. The velocity may be expressed in general in the form: $C=[(RT/M)(1+R/C_v)]^{\frac{1}{2}}$, which applies to pure gases or mixtures of gases that obey the perfect gas laws. In this relation T is the absolute temperature; M is the mean molecular weight defined as: $M=\Sigma M_i p_i/\Sigma p_i$, C_v is the specific heat (per gram molecule) defined as: $C_v=\Sigma(C_v)_i p_i/\Sigma p_i$, where the summation is taken for all the gas components present. In the case of the arc in air, the components considered are the undissociated and dissociated oxygen and nitrogen. The values for the specific heat and degree of dissociation, taken from the equilibrium calculations of H. L. Johnston and associates (J. Am. Chem. Soc. **55**, 153 (1933)), are used, care being taken to apply the correct partial pressures. Possible sources of error due to thermal diffusion and other causes are considered.

63. The Rotational Dispersion of Sound in Hydrogen. ANGUS S. ROY AND MORRIS E. ROSE, *University of Michigan.*—The problem of the dispersion of sound in hydrogen due to rotational energy lag is investigated. From the result of an order of magnitude calculation of the cross section for the excitation of rotation it is to be expected that such a dispersion would exist only at frequencies greater than 10^6 cycles per second. This prediction is entirely consistent with the result of the experimental work, which is that no dispersion is found in hydrogen up to a frequency of 1465 kilocycles per second at atmospheric pressure. In the dispersion region the sound velocity depends on the ratio of the pressure and the frequency; therefore, in order to avoid the use of many crystals, measurements were made at 388 kc and 1465 kc and at various pressures ranging from 424 to 772 mm Hg. The results showed a variation of less than one percent from the low frequency velocity of sound in hydrogen.

64. The Change in Thermal Energy Accompanying Change in Magnetization of Nickel. AGNES TOWNSEND, *Columbia University.*—The specimen, in the form of a wire 1 mm in diameter and 30 cm long, is placed axially in a cylindrical calorimeter about which a solenoid is wound. An array of thermocouples in thermal contact with the specimen permit changes in its temperature to be detected. The change in thermal energy which accompanies any change in magnetization is measured by comparing the concurrent change in temperature with that which appears when a known electric current passes through the specimen for a known time interval. As a specimen of nickel is carried through a half cycle of magnetization, commencing with maximum magnetization, the thermal energy decreases until (approximately) the knee of the hysteresis curve is reached. This is followed by a large increase as the steep part of the curve is traversed, and then by a much smaller increase as the half cycle is completed. The behavior of nickel is in contrast with that of carbon steel, for which Ellwood found an *increase* in thermal energy over the initial stage and a *decrease* over the final stage of this process.

65. A Magnetic Study of the Metallic State and the Fermi-Dirac Statistics. SIMON FREED AND HARRY G. THODE, *University of Chicago.* (*Introduced by A. J. Dempster.*)—The application of the Fermi-Dirac statistics to metals leads to a distribution of the spin of the electrons which does not vary much until about 40,000°C, the so-called critical temperature, is reached. Hence, magnetic measurements of metals which register the magnetism associated with the spin could scarcely serve as a test of the statistics since the variations in magnetism expected from the statistics would set in at such temperatures. However, on diluting a metal with a non-metal, a lowering of the critical temperature would be anticipated. When the metal in the diluted state occupies a volume of say 20,000 times as great as in the pure state, the distribution at room temperature is practically the same on the Fermi-Dirac statistics as on the classical statistics; the elementary magnets would be almost independent of each other. We have measured the magnetic susceptibilities of sodium dissolved in liquid ammonia at various concentrations, the dissolved metal occupying from 100 times to 20,000 times the volume of pure metal. The atomic susceptibility of sodium varied from that of the pure metal to about 100 times as much. In the most dilute solution measured, the atomic susceptibility was about two-thirds the para-

magnetic susceptibility which would arise from independent magnets having one-half unit of spin. The temperature coefficients of the susceptibilities will also be discussed.

66. Magnetoresistance in Sodium-Potassium Alloy. C. W. HEAPS AND J. E. ARMSTRONG, *The Rice Institute.*—It has been found by Fakidow and Kikoin (Phys. Zeits. d. Sow. **3**, 381 (1933)) that the liquid alloy NaK increases its resistance when subjected to a transverse magnetic field. This discovery has been further investigated using longitudinal fields and specimens of very fine diameter. Contrary to expectations it has been found that with tubes considerably finer than those used by Fakidow and Kikoin there appears to be a larger effect of tube diameter on magnetoresistance. A spurious effect due to motions in the liquid is thus shown to be present. However, a genuine, intrinsic effect is believed to exist. In a longitudinal field the magnetoresistance is larger than in a transverse field. To explain longitudinal magnetoresistance it is assumed that the field produces structural changes in atomic systems. For the liquid alloy, therefore, a magnetic field would seem to induce a pseudo-crystalline state. One point of view would be that the field is able to produce alterations in G. W. Stewart's cybotactic state. X-ray experiments are being performed to test this theory.

67. The Hall Effect in Sodium, Potassium and Caesium. F. J. STUDER AND W. D. WILLIAMS, *Union College.*—The Hall effect has been studied in carefully purified samples of sodium, potassium, and caesium obtained by distilling the metals in vacuum, into thin flat molds of Pyrex, with sealed-in electrical leads. The Hall constants determined are as follows: Sodium -0.0021, potassium -0.0042, and caesium -0.0078. The Hall effect in each case was found to be independent of the current density in the specimen, and of the magnetic field intensity. The effect of temperature was studied for potassium, and no variation in the Hall constant was noted over the range -15°C to 60°C. Attempts were made to follow the Hall e.m.f. from the solid to the liquid state, but the readings were always unsteady as the melting point was reached, so that no consistent data were obtained. The change in resistance due to the magnetic field was too small to observe, up to a field of 20,000 cgs units. The theory of Sommerfeld and Frank has been considered in connection with the alkali metals lithium and sodium, insufficient data being available for the others.

68. A New Balanced Circuit for Resistance Thermometers, Combustible Gas Indicators, etc. M. G. JACOBSON, *Mine Safety Appliances Company. (Introduced by A. G. Worthing.)*—A circuit is developed which is a cross between a potentiometer circuit and a Wheatstone bridge circuit: it can be regarded as a potentiometer circuit in which a part of the power source itself (one or more cells of a battery) instead of an independent e.m.f. is used to compensate the voltage drop through a part of the circuit fed by the power source; or it may be regarded as a Wheatstone bridge, in which the 2 parallel branches are replaced by 2 or more cells of the feeding battery. It is shown that this circuit is particularly advantageous for portable instruments, because it gives the same or even more sensitivity than a Wheatstone bridge with a much smaller current consumption. This circuit is successfully used in several instruments manufactured by the Mine Safety Appliances Company in Pittsburgh, in whose laboratories it was developed. For applications to hot wire combustible gas indicators, etc., it is important to maintain the temperature of the wire which is in one of the branches of the above circuit at a very constant value—against changes in e.m.f. and the wire itself. A simple circuit for this purpose is described. The mathematical proofs and details of both circuits are given in an appendix.

69. Rubber Deformations Caused by Uniformly Repeated Stresses. MILTON L. BRAUN, *Catawba College.*—If a rubber band of length l is stretched by a given force to $l+e$ its length when the stretching force is removed becomes $l+\Delta l$. If the same stress is applied a second time the elongation becomes $e+\Delta e$, and the first net stretch $s\ (=e)$ becomes $l+(e+\Delta e)-(l+\Delta l)=s+\Delta s$ for the second stretch, the relation between the increments being $\Delta s=\Delta e-\Delta l$. The effect of n isothermal applications of a given gravity load to an ordinary vulcanized rubber band was found to be:

$$(1)\ E=an^{\alpha},\quad (2)\ S=bn^{\beta},$$

$$(3)\ L=l+E-S=l+an^{\beta}(n^{\alpha-\beta}-b/a)=l+cn^{\gamma}$$

(empirically), where E is the elongation beyond the original length when the load has acted for one minute, S is the actual stretch produced by an individual application of the load, L is the length of the band measured one minute after the removal of the load, n is an integer representing the number of the consecutively repeated force, a, b, c, α, β, γ, and l are positive constants, l being the original length of the band. These equations have been established as a first approximation for several rubber compositions, for various loads and temperatures, and for values of n beyond a hundred. Further work is contemplated.

70. High Rotational Speeds in Vacuum. E. G. PICKELS AND J. W. BEAMS, *University of Virginia.*—The rotating member consists of three main parts: a small, conical, air driven, air supported turbine (see Beams, Weed and Pickels, Science **78**, 338 (1933)); a much larger and heavier rotor of any desired shape, which spins in the vacuum chamber; a steel piano wire extending vertically downward along the axis of rotation from the apex of the turbine above the vacuum chamber to the larger rotor which it supports and drives. The wire enters the chamber through a small hole that leaves a very slight clearance. Viscous oil slowly fed into this clearance both lubricates the bearing and serves to make it vacuum tight. The vacuum obtainable is apparently limited only by the slight vapor pressure of the oil. The rotational speed is limited only by the strength of the rotor—e.g.,—a solid duralumin rotor (450 grams, 9 cm diam.) exploded when the maximum centrifugal force reached approximately 900,000 times gravity. This larger rotor, even when considerably unbalanced, spins smoothly. Since friction losses in both the wire and the vacuum rotor are negligible, and since the vacuum pro-

vides a high degree of thermal insulation, the apparatus affords not only a most efficient centrifuge, but a means of investigating many different phenomena.

71. High Speed Electrical Motors. R. C. COLWELL AND N. I. HALL, *West Virginia University.*—Within the last two years, very high speeds approximating one million r.p.m. have been obtained with air turbines and gas driven centrifuges, but no electric motor heretofore has ever rotated faster than 32,000 r.p.m. Two types of high speed electric motors have been built which have actually rotated at 45,000 r.p.m. and are capable of withstanding the centrifugal force at 100,000 r.p.m. The first of these is a synchronous motor with a laminated rotor on a steel shaft rotating in ball bearings. This rotor has no d.c. winding and the laminations must be of a special shape. This motor is not self-starting but is synchronized at low speed and then brought up to full speed by raising the frequency of the applied current. The second type is an eddy current motor which consists of an aluminum disk mounted on a vertical shaft; it is pulled around by a rapidly rotating magnetic field. The rotating field is produced by a 500 cycle two phase generator which is run fifty percent over normal speed. By using vacuum tubes or a specially designed high frequency alternator it should be possible to attain much higher angular velocities.

72. Current-Voltage Relations in Blocking Layer Photo-Cells. LAWRENCE A. WOOD, *Cornell University.*—Observations have been made of current (0.1 to 10,000 μa) in a Weston photronic blocking-layer photo-cell, as a function of illumination (1 to 100,000 lux) and of potential difference across the cell. The use of a graph of current against voltage is discussed, with particular reference to the choice of an external resistance for maximum power output. The leakage current through the blocking layer has been calculated, and from it the d.c. conductance in the low-resistance direction is obtained. This consists of a constant conductance of the order of 80 micromhos, as well as two other terms, one varying approximately as the 0.8-power of the leakage current and the other as the 0.4-power of the illumination. In the dark a conductance as high as 20,000 micromhos may be obtained; this reaches about 30,000 micromhos with maximum illumination. Similar studies of the Westinghouse Photox cell indicate a much smaller variation of conductance with leakage current and a larger variation with illumination.

73. Temperature Effects on Photo-Voltaic Current and e.m.f. of a Selenium Mono-Crystal Platinum Film Combination. R. M. HOLMES AND L. C. WHITMAN, *University of Vermont.*—Lamellar crystals of selenium were grown in an evacuated tube by condensation of the vapor. Platinum films covering approximately half of each surface were deposited by sputtering. The combination was placed in a uniform temperature enclosure. Light transmitted through one of the films causes an electron flow from selenium to the illuminated film, then through an outside circuit returning to the non-illuminated film. The magnitude of the current depends upon temperature. From −20°C to 50°C there is a reversible and nearly linear decrease, the rate at 50°C being −4 percent per degree. Between 50°C and 100°C the decrease is smaller, reversible and non-linear while exposure to higher temperatures results in a permanent decrease caused by baking of the platinum films. By e.m.f. is meant the opposing *p.d.* introduced into the outside circuit to stop the current. This decreases linearly and reversibly from −20°C to 20°C at approximately 0.5 millivolt per degree. The decrease is reversible but smaller and non-linear up to 100°C. Baking of the films during exposure to higher temperatures causes a permanent decrease. These effects are described by a theory which relates the current and e.m.f. to resistances in the combination either reversibly or permanently changed by heating.

74. Loss and Restoration of Photo-Conductivity in Red Mercuric Iodide. FOSTER C. NIX, *Bell Telephone Laboratories, Inc.*—Single crystals of red mercuric iodide, which normally display photo-sensitivity when precipitated, lose their photo-sensitivity on aging. This loss is accompanied by a change from the mono- to the polycrystalline fibrous state with considerable randomness of orientation of the individual crystallites. The non-sensitive crystals can be resensitized by subjecting them to an electric field for a time of the order of a few minutes. The rate of resensitization and the magnitude of the attained photo-sensitivity are found to increase with (a) increase in applied field strength and (b) decrease in temperature. When the light is turned on the photoelectric current is found, under certain circumstances, to rise briefly to a maximum and then descend to a permanent value at which the total current is equal to the value of the dark current prevailing when the voltage was first applied.

75. Diffusion of Hydrogen through Iron and Palladium. W. R. HAM AND J. D. SAUTER, *The Pennsylvania State College.*—As previously reported* the diffusion rate of hydrogen through palladium may be greatly modified by heat treatment of the palladium in various atmospheres. This is also true of iron. In general the apparent mass action law for diffusion of hydrogen through these two metals depends on rate alone; i.e., a sample of fresh palladium may be degassed until at 300°C and 760 mm pressure the rate is a certain amount, another sample may require heating to 600°C at 760 mm pressure to obtain same rate. The flow equations of both will be identical insofar as pressure changes at these temperatures are concerned. Iron exposed to nitrogen may have its diffusion rate for hydrogen increased 10 to 15 times, but after baking out at higher temperatures the diffusion curve comes back to its original position. Diffusion isotherms for Fe and Pd and very slow rates always approach $R_1 = A_1 p^{1.0}$; for very high rates, $R_2 = A_2 p^{.5}$. There is an apparently continuous variation from one exponent to the other.

* Phys. Rev. **45**, 741 (1934).

76. The Expansion of Copper from Absolute Zero to Its Melting Point. W. J. HARING AND WHEELER P. DAVEY, *Pennsylvania State College.*—The total expansion of copper was measured from 75°K to 1356°K and the curve was

extrapolated to 0°K. The total expansion from 0°K to the melting point was thus found to be 3.01 percent of the length at 0°K. This is consistent with the theory of melting of face-centered cubic materials (Davey, Phys. Rev. **27**, 319 (1926)) and with the spherical "shape" attributed to the atomic domain of such materials. The expansion over the whole range from 0°K to 1356°K is given by $L=L_0(1+\alpha t)$ where α lies between 2.24×10^{-5} and 2.35×10^{-5}. It is given still more accurately between 200°K and 1200°K by $L=L_0(1+\alpha t+\beta t^2)$ in which α and β are 2.26×10^{-5} and -2.44×10^{-9} respectively between 200°K and 500°K and 2.08×10^{-5} and 1.66×10^{-9} respectively between 700°K and 1200°K.

77. Technique for Making Sound Ingots for Density Determinations. P. G. WALDO AND WHEELER P. DAVEY, *Pennsylvania State College.*—Pure copper was melted by means of a gas flame in alundum crucibles inside an evacuated ("satin") quartz tube. At room temperature the pressure inside the tube was 0.004 mm. At 1080°C the pressure rose to 1 mm in spite of continuous pumping by means of a Cenco Hyvac pump. Surprisingly this low pressure of gas was enough to give visible gas pockets in the copper and the lattice parameter was different from that of pure copper. When the quartz tube was surrounded by a second quartz tube evacuated by a second Cenco Hyvac pump, the pressure in the inner tube only rose to 0.02 mm and copper of normal density (8.994±0.004) was obtained. It is thought that, if the above technique had been observed by Phelps and Davey (A.I.M.E. Tech. Pub. 443), their results would have been different.

78. Representations and Ray Representations in Quantum Mechanics.* J. VON NEUMANN, *Institute for Advanced Study, Princeton, N. J.*

79. Symmetry Relations in Various Physical Problems.* E. WIGNER, *Princeton University.*

80. Some Applications of Group Theory to Non-Relativistic Problems.* J. H. VAN VLECK, *Harvard University.*

81. Some Applications of Group Theory to Dirac's Relativistic Theory.* G. BREIT, *University of Wisconsin.*

82. The Electrical Phenomena of the Cochlea and the Auditory Nerve.* HALLOWELL DAVIS, *Harvard Medical School.*

83. The Absorption of Sound in Gases.* VERN O. KNUDSEN, *University of California.*

84. Some New Instruments of Acoustical Research.* E. C. WENTE, *Bell Telephone Laboratories, Inc.*

85. The Stark Effect in the Hydrogen Isotopes. J. S. FOSTER AND A. H. SNELL, *McGill University, Montreal.*—The Stark effects for the first four members of each Balmer series have been photographed from a Lo Surdo source containing a mixture of the isotopes. Each observed asymmetric Stark intensity pattern for deuterium is nearly the mirror image of the corresponding hydrogen pattern. Similar results are obtained with a canal-ray tube which operates at unusually high pressures. The observed low total intensity of each Balmer line at the point corresponding to the first application of the external field in a Lo Surdo source is thought to be due to additional collisions arising from the dipole forces which are abruptly and completely developed at this point. Variations from the regular Epstein spacing of deuterium components are found to be in fair agreement with the Schlapp theory of the fine structure of the Stark effect.

(To be called for immediately following paper No. 86)

86. X-Ray Measurement of Depth of Cold Work. CHARLES S. BARRETT, *Carnegie Institute of Technology.*—Spots on Debye rings from a metal lose distinctness when the metal is cold worked. The depth of a cold worked layer on the surface of a metal may be determined by a series of photograms using non-penetrating x-rays. Each photogram is made with a different thickness of metal removed from the surface by etching. The method is direct and sensitive. It finds a practical application in the recently developed technique of surface cold-rolling of shafts to increase their endurance to alternating stresses. A fatigue specimen of axle steel (0.42 percent C), whose surface was cold worked by rollers of 2" diameter and 1½" contour radius which were pressed against the specimen by a 400 lb. radial force, was studied by this method. The specimen proved to have been cold worked to a depth of 0.055"±0.005. X-ray penetration into the specimen was negligible; reflections from (310) planes with cobalt radiation were used in a back reflection camera. R. E. Peterson, who furnished the specimen, predicted about 0.067" for the depth in this instance, on the basis of a stress distribution under the rolls as calculated by Thomas and Hoersch.

(To be called for immediately following paper No. 52)

87. Determination of the Sign of Nuclear Magnetic Moments by the Method of Atomic Beams. I. I. RABI, *Columbia University.*—The sign of the nuclear magnetic moment with respect to its angular momentum can be inferred from the hyperfine structure by observing whether the hyperfine structure multiplet is normal or inverted. In molecular beam experiments there is no such criterion due to the symmetry in the magnetic moments of the different magnetic levels. Since such information would be of interest with regard to the proton and deuton moments a method is proposed in which a single magnetic level is sorted out of the beam and sent through a very weak inhomogeneous field in such a manner that non-adiabatic transitions occur to other magnetic levels. When the beam is analyzed subsequently in another magnetic field the sign of the nuclear magnetic moment may be deduced from the resultant states of the atoms.

(To be called for immediately following paper No. 59)

* Invited papers.

88. Frequency and Magnitude of Cosmic-Ray Showers as a Function of Altitude. RALPH D. BENNETT, GORDON S. BROWN AND HENRY A. RAHMEL, *Massachusetts Institute of Technology.*—Preliminary measurements of the magnitude and frequency of cosmic-ray showers have been made at each of four elevations: 170 meters, 1620 meters, 3100 meters and 4300 meters, for periods of time extending from 189 to 336 hours. One of the new cosmic-ray intensity meters of the Carnegie Institution was used in making the measurements, and only showers involving more than about 100 particles passing through the ionization chamber have been considered. Analysis of the frequency of arrival of showers as a function of their magnitude indicates that there are at least three classifications of showers at each location. The observations at the lowest level were made indoors under a slate, steel and concrete roof while the others were made in a tent. The observations made indoors indicate a deficiency in showers corresponding to less than about 500 particles passing through the chamber. The frequency of arrival of showers, taking all sizes above about 100 particles into account, increases somewhat faster with increase in elevation than does the absolute value of cosmic-ray intensity. The shower frequency curve extrapolated to single-ray showers and integrated to give the total ionization due to showers indicates that showers obeying the frequency laws derived contribute only a small fraction of the total ionization. A few showers of very great magnitude were observed at each level, their magnitude increasing rapidly with altitude. At the 4300 meter level three showers were observed which threw the instrument off scale, the largest of which produced not less than 10^9 ion pairs, indicating not less than 5000 particles passing through the chamber and an energy release in the chamber (probably a small fraction of the total) of not less than 3×10^{10} electron volts. The relationships derived for the time intervals between showers indicate that they arrive in a random manner.

(To be called for immediately following paper No. 7)

89. On the Principle of Uncertainty in Sound. WINSTON E. KOCK, *University of Cincinnati.* (*Introduced by L. T. More.*)—Following Stewart, a discussion of the applicability of the principle of uncertainty ($\Delta\nu\Delta t\approx 1$) to sound phenomena is given. Various sound phenomena are thereby explained and certain related experiments with frequency vibrato are reported. The phenomena explained are: the chromatic glissando imitation of a portamento, analysis of a formant into a Fourier series, the relation between vibrato wideness and pitch range, and the pleasing effect of a frequency vibrato.

(To be called for immediately following paper No. 68)

90. The Inductive Glow Discharge Oscillator. WINSTON E. KOCK, *University of Cincinnati.* (*Introduced by L. T. More.*)—An analysis of the intermittent glow discharge oscillator with inductance inserted in the condenser arm and operating in the neighborhood of resonance frequency is presented. The production of oscillations of the first and second kinds and the application of an overdamped oscillator in producing formants is discussed.

(To be called for immediately following paper No. 89)

91. Wave Mechanical Treatment of the LiH Molecule. JULIAN K. KNIPP, *Harvard University.*—A variational treatment of the LiH molecule has been carried out in which the two electrons of the inner shell of the Li atom are represented by Slater wave functions and the orbitals of the two valence electrons are treated after the method of James and Coolidge (but without the internuclear distance as one of the coordinates). In this treatment elliptical coordinates are used for the expression of the outer electron function, which takes the form of an exponential times a power series. A calculation made at the experimental equilibrium internuclear distance of the ground state, a distance of three Bohr radii, gives with eleven terms in the series a binding energy of 1.77 e.v., to be compared with the experimental value of 2.56 e.v. The addition of two terms containing the cosine of the difference of the azimuthal angles of the two outer electrons brings the binding energy to 1.90 e.v. An examination of the contributions to the energy of individual terms seems to indicate that several more terms of both sorts might give further reduction of approximately 0.2 e.v. A parallel treatment of the LiH ion carried out at an internuclear distance of three Bohr radii gives for the lowest state a repulsion of 0.19 e.v. with excellent convergence.

92. The Production of Cosmic-Ray Showers by Lead at Different Elevations. D. D. MONTGOMERY AND C. G. MONTGOMERY, *Bartol Research Foundation of the Franklin Institute.*—The rate of occurrence of bursts of ionization in a fifty liter Dow metal ionization chamber filled with nitrogen at 200 lbs. pressure, produced by 140 lbs. of lead shot placed over it has been measured at the summit of Pike's Peak (14,109 ft.), Glen Cove (11,425 ft.) and Colorado Springs (6098 ft.). From Colorado Springs to Pike's Peak the number of bursts greater than 1.5 million ions due to the lead increases by a factor of about nine. This increase corresponds to an absorption coefficient of 0.9 ± 0.1 per meter of water if it is assumed that the absorption may be represented by the Gold integral. The production of bursts must then either be due to a very soft component of the cosmic radiation or else some mechanism for their production similar to that proposed by W. F. G. Swann (Phys. Rev. **46**, 828 (1934)) must be supposed.

93. The Longitudinal Motion of a Long Coil Spring Suspended Vertically from a Rigid Support. D. A. WELLS, *University of Cincinnati.* (*Introduced by L. T. More.*)—A general solution for the longitudinal motion of a long coil spring suspended vertically from a rigid support has been obtained. The variation in mass per unit length has been taken into account and displacements as a function of time are determined from the stretched equilibrium position. It was found that the differential equation involving displacement from the equilibrium position could be thrown into the usual wave equation by a proper change of variables. Particular solutions for typical boundary conditions (lower end free, lower end loaded and lower end fixed) are given.

94. Transverse Vibrations of Long Rods. ISAY A. BALINKIN, *University of Cincinnati.* (*Introduced by S. J. M. Allen.*)—An expression is derived by the use of calculus only giving the fundamental frequencies for long rods fixed at one end and vibrating alone or with a concentrated load at the free end.

$$\nu=(1/2\pi)\{3EIg/(W+0.236W_1)l^3\pm 3g/2l\}^{\frac{1}{2}}.$$

When the axis of the blade is horizontal, the term $3g/2l=0$. When the free end of the blade is below the support—"elastic pendulum," the term $3g/2l$ is added and it is subtracted when the free end is above the support. For this position $\nu=0$ when the two terms under the radical become equal. The maximum concentrated load that a long rod can carry is then $W=2EI/l^2$ which is 20 percent below the value given by the classical Euler's formula for columns, $W=2.5EI/l^2$. Experimental curves are shown to compare favorably with the theoretical deductions for all cases considered.

95. The Magnetic Moment of the Potassium K^{39} Nucleus. J. J. GIBBONS AND J. H. BARTLETT, *University of Illinois.*—Starting with the K^+ field given by Hartree, a $4s$ wave function has been found by numerical integration. The orthogonality correction diminishes the value of the wave function at the origin by about one-third. The experimental value of the hyperfine structure separation of the ^3S normal state is 0.015 cm^{-1}. This results in a nuclear magnetic moment of 0.10 nuclear magneton, as compared with the value of 0.38 nuclear magneton calculated by Millman, Fox and Rabi (Phys. Rev. **46**, 320 (1934)) on the basis of the modified Goudsmit formula.

96. The Energy Levels of the Asymmetrical Rotator in the New Quantum Theory. ENOS E. WITMER, *University of Pennsylvania.*—The Hamiltonian for the asymmetrical rotator can be written in the form:

$$H=\tfrac{1}{2}ap^2+\tfrac{1}{2}(c-a)H'(s;\theta,\phi,\psi,p_\theta,p_\phi,p_\psi),$$

where a, b and c are the reciprocals of the principal moments of inertia, p is the total angular momentum, θ, ϕ, ψ, p_θ, p_ϕ, p_ψ are Euler's angles and the conjugate momenta, and

$$s=(b-c)/(a-c).$$

The a, b and c do not appear either in p or H'. For convenience take $a>b>c$. Then it can be demonstrated that the energy levels E can be written in the form:

$$E=(h^2/8\pi^2)j(j+1)\{a+(c-a)\tau(s;n,j)\}.$$

This formula is analogous to a similar formula in the old quantum theory. Here n is the second quantum number. Since τ depends merely on one parameter s besides n and j, it becomes feasible to tabulate τ, and this has been done in part by the author. Furthermore,

$$\tau(1-s;-n,j)=1-\tau(s;n,j).$$

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